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A Review of Developments in Vacuum Research and Engineering

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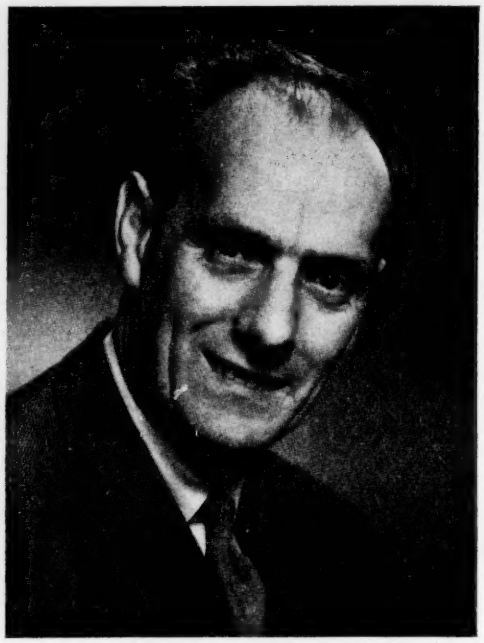

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Mr. Yarwood was born in 1913 in London. At the age of 19 he entered the Research Laboratories of Electric and Musical Industries Ltd., Hayes, Middlesex, as an assistant engaged on research into beam-tetrode valves, television pick-up tubes and image converter tubes. At the same time he undertook studies in evening classes at the Sir John Cass College towards the London B.Sc. Special Physics degree and was awarded Honours in the 1940 examinations. Subsequently, he was awarded the Master of Science degree of London University for a dissertation on electron optics. After a period of two years as a research physicist at Adam Hilger Ltd., where he specialised in vacuum coating techniques, he was appointed as lecturer to Royal Air Force trainees at the Sir John Cass College. From 1944 to 1948 he was a lecturer in Physics at the S.E. Essex Technical College, Dagenham; subsequently, he was appointed as Senior Lecturer in Physics at the Polytechnic, Regent Street, London, and became promoted to Head of Department in 1953.

In 1943, his book 'High Vacuum Technique' was published by Chapman and Hall Ltd. It is now in its third edition and has also been translated into German and Serbo-Croatian. He has recently written a two-volume work, with Dr. J. H. Fewkes of the Polytechnic, entitled 'Electricity, Magnetism and Atomic Physics', the first volume of which was published in 1956. A few months ago, Mr. Yarwood accepted an offer to serve on the Editorial Board of 'Vacuum'.

At the Polytechnic, apart from pre-occupation with both day and evening students preparing for degrees in mathematics and physics, he is engaged (with post-graduate students) on research, the present topic being concerned with fundamental investigations into the production and measurement of ultra-high vacua.

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EDUCATION IN VACUUM PRACTICE AT COLLEGES OF THE UNITED KINGDOM

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Summary

DETAILS ARE GIVEN OF THE FACILITIES available at the universities and technical colleges in the United Kingdom for education in vacuum technology and of the way in which the instruction fits into the courses in science and engineering. The differences in approach to training in the universities and the technical colleges are considered. The courses offered are criticised on the grounds that, at the university, the instruction is too meagre at the undergraduate level and only the post-graduate student undertaking research for the Ph.D. obtains any real appreciation of vacuum techniques, whereas, at the technical colleges, the lectures and laboratory practice are often insufficiently concerned with fundamentals and inadequately critical in approach.

Sommaire

DÉTAILS SUR LES FACILITÉS apportées à l'étude des Techniques du Vide dans les Universités et Collèges Techniques du Royaume Uni, ainsi que sur la manière d'introduire cette étude dans les cours de sciences et de mécanique. Les cours ainsi donnés sont critiqués dans le sens où l'instruction sur le Vide dans les Universités n'est pas assez élevée pour les étudiants non diplômés et que seulement les étudiants diplômés et poursuivant leur études pour obtenir le Doctorat de Physique peuvent réellement étudier les techniques du Vide. De mème pour les Collèges Techniques, les conférences et travauz pratiques sont trop superficiels.

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INTRODUCTION

DR. ANDREW GUTHRIE† has published an interesting survey of the educational activities in the field of vacuum practice at universities, institutes of technology, industrial establishments and government research departments in the U.S.A. Summarising, he states that the most widespread method of training is of the 'on-the-job' variety, involving working with vacuum equipment and with more experienced personnel, the use of informal conferences and the use of technical literature. Complete courses of instruction in vacuum technology, in universities or industry, are quite rare.

A similar state of affairs obtains in the universities of Great Britain. The undergraduate who takes an honours course for the B.Sc. Special in Physics, is asked to conduct a few experiments on small vacuum plant, is taught the fundamentals of the kinetic theory of gases at low pressures in a lecture course on the properties of matter and will only acquire some real appreciation of the importance of vacuum practice when studying atomic physics and electronics. As far as undergraduate courses in electrical or mechanical engineering are concerned, it is not uncommon to find that the student is not required to do any experimental work at all involving vacuum

* MS. received January, 1958.

† Guthrie, A., 'Vacuum Education in the U.S.A.' *Vacuum*, **5**, 5.

plant; despite the overcrowding of syllabuses it would seem there is scope for improvement here. Finally, in the case of chemical engineering and metallurgy courses, the high cost of equipment forbids the provision of more than small pilot plants.

Thus, an opportunity for proper appreciation of the construction problems which present themselves when setting up and operating vacuum apparatus occurs only when the graduate joins industry or, alternatively, elects to carry out post-graduate research for the Ph.D. in subjects such as electron-optics, atomic and nuclear physics, low-temperature physics, ionisation phenomena in gases, heat transfer and solid-state physics. Therefore, in this country as well as the U.S.A., the chief method of training is of the 'on-the-job' variety.

On the other hand activities covering vacuum engineering proper are becoming increasingly popular in the technical colleges of Great Britain as distinct from the universities. This is particularly pronounced in the case of the courses in applied physics newly instituted for the Diploma in Technology (Dip. Tech.) and, to a lesser extent, in the case of part-time courses for the National Certificate in Applied Physics. Here again, training in vacuum practice is largely the prerogative of the physics student, though the student of mechanical engineering, chemistry or metallurgy also gains some knowledge of the subject in ancillary physi s courses. Furthermore, some of the colleges have arranged special courses in vacuum practice. Of the latter there are three types: (*1*) Evening Courses, (*2*) part-time day courses and (*3*) short full-time courses which last from one to two weeks. The university graduate who has entered industry or even the post-graduate student engaged in research work for his Ph.D. at the university often avails himself of this opportunity to supplement his necessarily limited 'on-the-job' experience in vacuum techniques.

SURVEY OF TRAINING FACILITIES

In order to obtain a more detailed picture of the educational facilities available in this field, universities and technical colleges in Great Britain have been invited by the author to report briefly on their programmes. The following notes are based on these reports. This survey is not necessarily complete but can be taken as representative of conditions in this country. The various educational institutes are listed in alphabetical order of their location and/or of the areas they serve.

Aberdeen University

Undergraduate students in the Department of Natural Philosophy, preparing for an Honours degree in Physics, acquire some experience of vacuum practices in the third year of the four-year full-time course. The practical work comprises a few experiments involving the use of diffusion pumps and, by way of example, one of these is concerned with the variation of the viscosity of a gas with pressure.

Post-graduate students are in a better position to acquaint themselves with vacuum practice as they make considerable use of vacuum apparatus in research work on thin films, low temperature physics and other branches of physics where the problem investigated is not specifically that of vacuum.

Brunel College of Technology

Acton

The college offers three courses embracing vacuum practices.

Diploma in Technology in Applied Physics. This is a four-year full-time (sandwich) course. In the second and the third year the schedule provides 20 one-hour lectures and practical work lasting from 10-20 hours. In the fourth year the student is engaged in project experiments involving vacuum practices.

Higher National Certificate in Applied Physics. This is a part-time course extending over two years and consists of 11 three-hour periods each comprising a one-hour lecture and two hours devoted to practical work.

Basic High Vacuum Technology. This is a special course planned to take place once a year but whenever there is sufficient demand it is arranged to take place more frequently. The course consists of 12

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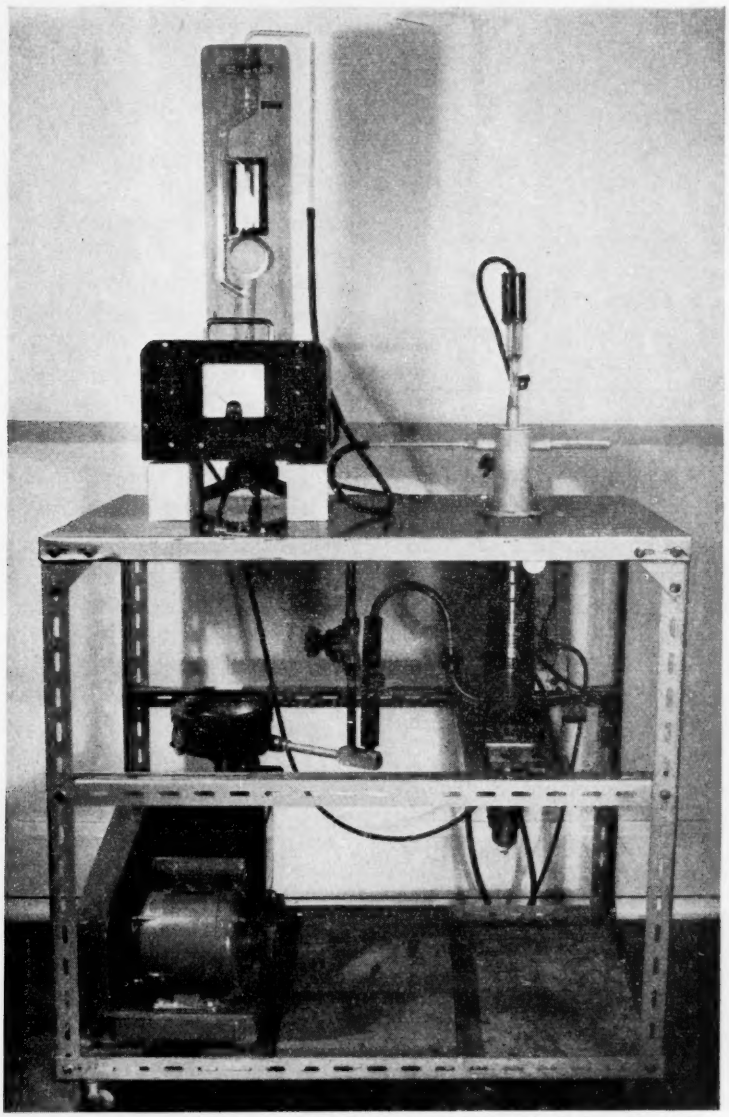
Vacuum in Training the Undergraduate I.



by Courtesy of College of Technology, Birmingham

Fig. 1 Two-decker trolley for students' experiments at College of Technology, Birmingham. On the lower deck, a rotary pump and diffusion pump are assembled; on the upper deck, the particular experiments are arranged. Facilitates storage and easy connection to electrical supplies and water tap. Every trolley is different to extend experience of students in handling equipment from various manufacturers.

three-hour periods, each comprising a one-hour lecture and two hours devoted to practical work as before.

The above courses are based on the syllabus given below.

Naturally, in the case of the part-time courses a selection has to be made from the topics shown.

(*a*) Flow of gases through tubes and orifices at low pressures, including relevant kinetic theory, derivation of simpler conductance formulae, concepts of pump speed, volumetric and mass-throughput, theoretical speed of vapour pumps, and Ho coefficient.

(*b*) Rotary pumps, gas-ballasting, measurement of pump speed, diffusion pumps (fractionating and self-purifying types), boosters and matching vapour pump to fore pump.

(*c*) Assembly of vacuum systems, introducing various accessories such as traps, isolation valves, etc.

(*d*) Vacuum gauges of the McLeod, Pirani, thermocouple and Knudsen type; cold and hot-cathode ionisation gauges; the alphatron gauge.

(*e*) Leak detection; various methods including differential methods and the mass spectrometer method.

(*f*) Materials used in vacuum engineering.

(*g*) Vacuum processing: Deposition of films of metals and dielectrics, interference filters; normal and reactive sputtering; gettering; freeze drying and distillation including molecular distillation.

University College of North Wales
Bangor

The information received covers the activities of two departments.

In the Physics Department the student reading for the ordinary degree is asked to carry out an experiment involving the use of a vacuum pump and a McLeod gauge. For example, he correlates the appearance of a discharge tube glow with the pressure in the system. In the Honours course such measurements are extended to cover the use of the Pirani and ionisation gauges.

In the Department of Applied Electricity the research student has an opportunity of gaining considerable experience while employing vacuum equipment for the exhaustion and activation of thermionic valves.

Queen's University
Belfast

No formal training in vacuum practice is provided in the Department of Physics. The Honours student receives some instruction from a professional glass-blower and the research student receives training of the 'on-the-job' variety. The latter applies in particular to those who join the post-graduate team concerned with the study of gaseous discharge phenomena generally and electrons in gases in particular.

University of Birmingham

Here vacuum practices form part of the programme of the Honours course in Physics. In the first year simple demonstrations of the operation of vacuum apparatus are given. In the second year, the students are required to carry out practical experimental work such as the study of the variation of the thermal conductivity of a gas with pressure in a Pirani gauge and, in the final year, three or four experiments involving vacuum apparatus are arranged.

Experiments on vacuum technique proper are: (*1*) Investigation of the effect of contaminating gases present at a certain partial pressure on a mercury discharge; (*2*) the calibration of an ionisation gauge against a McLeod gauge for both air and hydrogen and (*3*) the measurement of the pumping speed of a glass mercury diffusion pump.

Other experiments involving vacuum apparatus are concerned with x-ray apparatus and the β-ray spectrograph. It is contemplated increasing the number of vacuum experiments so far scheduled.

The particle accelerator projects undertaken in that department give valuable experience to post-graduate students engaged in research work with this apparatus.

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Birmingham College of Technology

Apart from a few basic experiments on vacuum technique undertaken in undergraduate courses for the B.Sc. Special Physics degree and also the Diploma in Technology in Applied Physics, the Department of Physics offers a post-graduate course in Vacuum Technique. This is an evening course of two terms (25 weeks) duration and covers kinetic theory, basic theory of high vacuum systems, production, maintenance and measurement of high vacua, and applications including electronic tubes and vacuum coating.

The experimental side of the course is being extended all the time. At present in this, as well as in a separate (electronics) course, the student assembles a triode valve from its components and, in addition, carries out all the auxiliary processes needed such as pumping, gettering and activation. Each experimental station is situated on a trolley which has two decks, the lower deck carries the evacuation plant consisting of a rotary and a diffusion pump and the upper deck is fitted with the actual experimental apparatus. Each experimental station is constructed from components of a different make in order to give the students an opportunity of gaining experience in handling apparatus from various manufacturers.

Brighton Technical College

Theory and practice of vacuum techniques are taught in the Physics Department to students attending the following courses: (*a*) The full-time and the sandwich course in Pure and Applied Physics, (*b*) the part-time Higher National Certificate course in Applied Physics, (*c*) the ancillary Physics course for the B.Sc. Special Degree in Chemistry, (*d*) the full-time Diploma course in Electrical Engineering and (*e*) the part-time Higher National Certificate course in Electrical Engineering.

Bristol University

Certain aspects of vacuum physics are dealt with in lectures forming part of the Honours course in physics and one or two experiments undertaken in the laboratory during that course but the chief training in vacuum technique is reserved for the post-graduate students who are asked to tackle a variety of research tasks requiring the use of the up-to-date vacuum equipment available in that department.

Cambridge University

The Department of Physics (The Cavendish Laboratory) provides for a vacuum experiment in the practical course of the final year of the Tripos. This experiment is of an optional nature and is confined to the use of apparatus consisting of a glass diffusion pump unit, McLeod, viscosity, and Pirani gauges. In the post-graduate research school vacuum equipment is employed in a wide variety of studies but in the Department of Chemical Engineering there are no special courses offered on vacuum techniques.

Welsh College of Technology
Cardiff

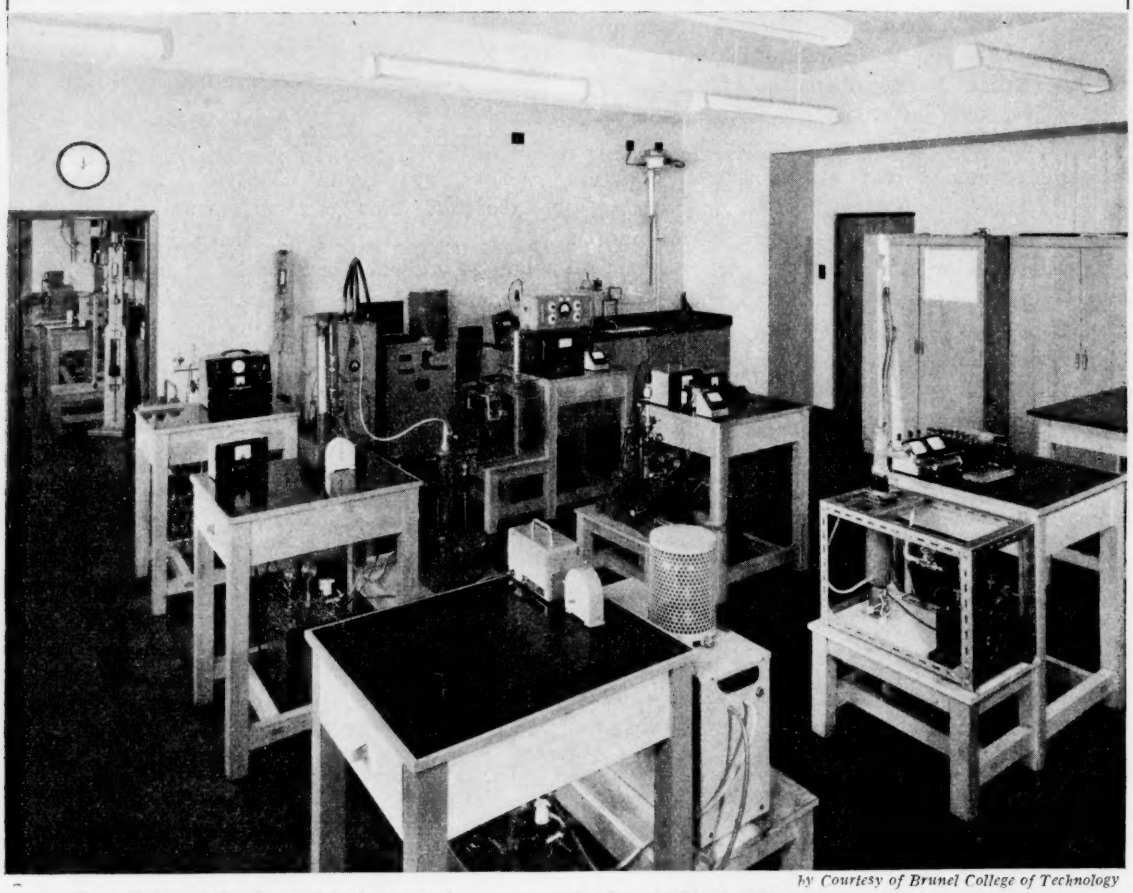
The Department of Applied Physics is equipped with four semi-permanent pumping stations, each monitored by thermo-couple, Pirani and ionisation gauges. Two of these stations are used for research and the other two are available for experimental work by students covering the production and measurement of high vacuum as well as straightforward processing techniques comprising vacuum coating such as lens blooming.

South-East Essex Technical College
Dagenham

The Department of Physics and Mathematics includes an x-ray and high vacuum laboratory which is equipped with several pumping stations for the use of students in their experimental work. An industrial evaporation plant is also available for research on interference filters and for the preparation of mirrors of the type incorporated in routine optical equipment. A list of typical experiments as carried out by the students is given as follows:—

The measurement of exhaust time and speed with a rotary pump; comparisons of calibration of different gauges, with moist and dry air; production of fully and semi-reflecting mirrors; production of anti-

Vacuum in Training the Undergraduate II.



by Courtesy of Brunel College of Technology

Fig. 2 Laboratories for students' courses in vacuum technology in Physics Department. Various experiments on rotary pumps, diffusion pumps, vacuum gauge calibration, leak-finding, measurement of tubulation conductance, etc. are arranged on separate small benches with rotary pumps on floor or on auxiliary low bench.

reflection films; observations on the effect of tubulation on pumping speed; measurements on getters.

In addition there are evening courses in valve technology and advanced practical physics, both of which include vacuum practice, and, finally, a special evening course in high vacuum techniques.

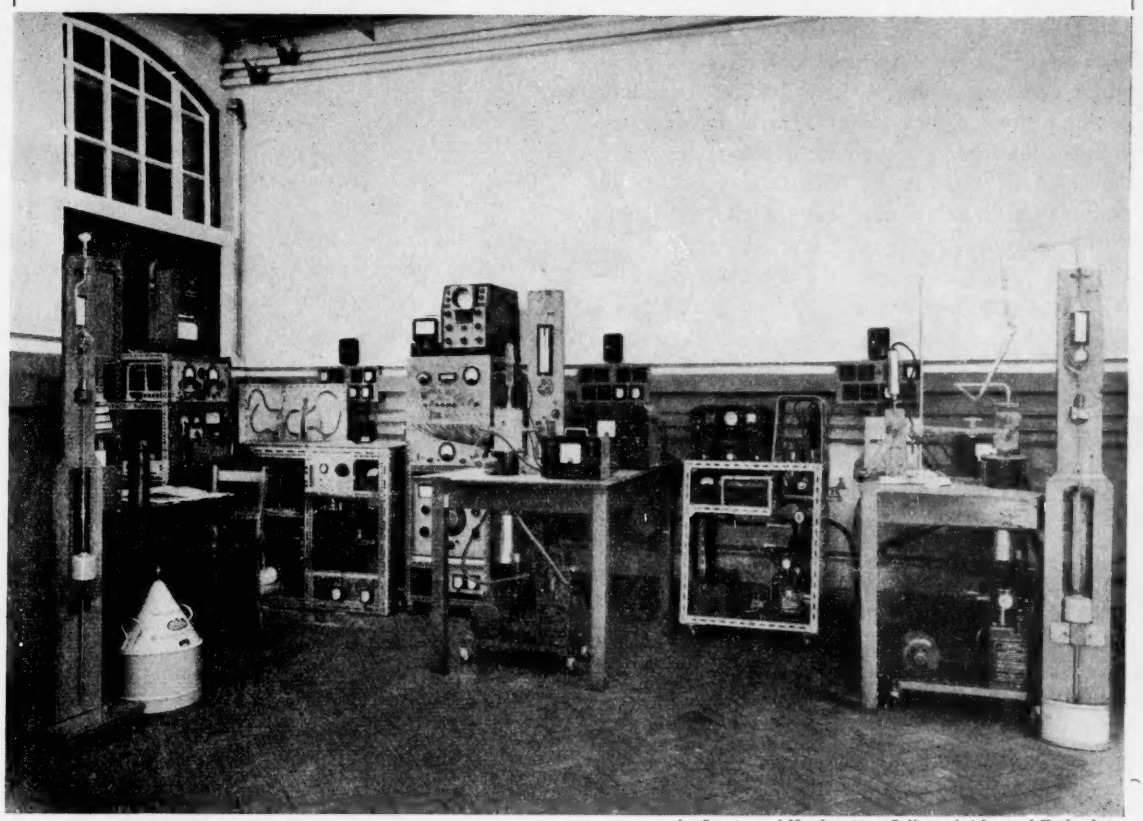
Queen's College of University of St. Andrews
Dundee

The Department of Physics provides no regular instruction in vacuum practice for undergraduates. However, vacuum technology is referred to in connection with the treatment of special subjects such as x-rays, electrical discharge phenomena, etc. The post-graduate research student, on the other hand, will obtain some practical experience during work with high vacuum equipment.

Heriot-Watt College
Edinburgh

The Physics Department offers two courses on vacuum physics, one for the benefit of full-time students preparing for the Associateship in Applied Physics, the other in the form of a special course for

Vacuum in Training the Undergraduate III.



by Courtesy of Northampton College of Advanced Technology

Fig. 3 Vacuum laboratory in Physics Department for training full-time and sandwich-course students preparing for the Diploma in Technology in Physics or Engineering or B.Sc. Engineering. Also used for special short courses for part-time students from industry.

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evening students. There are two pumping stations in the laboratories which are designed to be as flexible as possible in their application. Practical experiments cover procedures such as the calibration of the various types of vacuum gauges, the determination of pumping speeds, vacuum conditions in thermionic valves and the preparation of thin films.

The lectures cover a somewhat wider field and include:—

Kinetic theory and its application to gas equilibrium and flow at low pressures; measurement of vacuum, construction and principles of vacuum systems; vacuum materials; seals; leak-finding techniques; vacuum coating, distillation, simple vacuum metallurgy and vacuum dehydration.

Exeter University

Undergraduate students preparing for the Honours degree in Physics attend lectures and experiments on the construction of high vacuum apparatus and measurement practice. Post-graduate research students acquire considerable experience with vacuum equipment in their programmes of work. It is contemplated to establish special post-graduate courses in vacuum electron physics.

Glamorgan Technical College

The Physics and Mathematics Department teach vacuum techniques in connection with vapour pressure measurements and research into gas flow under conditions typical for mining. There is an additional special course in applied physics incorporating work on vacuum techniques in the sphere of electronics and telecommunications. Finally, facilities are provided for the training of chemical engineers in vacuum techniques as applied to distillation, evaporation and filtration.

Glasgow University

Undergraduates taking the Honours degree course in the Natural Philosophy Department attend four lectures on high vacuum practices. The experimental work is concerned with five different problems necessitating the use of vacuum equipment and offering experience in the operation of diffusion and rotary pumps as well as the manipulating of McLeod gauges.

The Department, being equipped with a synchroton, which is served by a fully automatic vacuum plant, post-graduate research students gain considerable 'on-the-job' experience.

Mention should be made of a special course for junior technicians essentially designed for the staff employed in the Department and consisting of nine lectures which last ninety minutes each. The following gives details of the syllabus:—

> Characteristics of rarefied atmospheres; molecular mean free path; outline of general features of pumping systems; measurement of pressure; open and closed manometers, the Lloyd, McLeod, Bourdon, Pirani, thermo-couple, ionisation and Philips gauges; rotary pumps, diffusion pumps, joints and taps; construction of systems; moisture traps; degassing procedures; leak-detection methods: discharge tube and palladium ion gauge, Lloyd leak indicator, mass spectrometer; evaporation and sputtering technique; survey of the Department's vacuum systems, including that serving the Glasgow synchrotron.

*Dr. F. E. Hoare, of the Department of Physics, is the member of staff most concerned with vacuum techniques. His comments are interesting:

Royal College of Science and Technology
Glasgow

The Department of Natural Philosophy provides a full-time four-year course in Applied Physics leading to the Associateship of the College which includes several lectures on vacuum practice and experiments in a well-equipped vacuum physics laboratory. The vacuum physics syllabus covers:

> Kinetic theory; vacuum gauges, rotary and diffusion pumps; measurement of pumping speeds; leak detection; evaporation and sputtering. Applications include electron microscopy, electron diffraction and x-ray techniques.
>
> In addition, vacuum equipment is used in research.

The Technical Chemistry and Metallurgy Departments of the College also have some vacuum equipment, but do not provide specific lecture courses on vacuum physics except where the student reads physics as an ancillary subject.

Huddersfield Technical College

Some of the experiments arranged for the normal degree courses of the Department of Physics and Mathematics involve the use of vacuum apparatus, *e.g.* investigations into variation of the electrical discharge with pressure and the determination of the charge-to-mass ratio of the electron. Engineering students reading for the Higher National Diploma measure pumping speeds and become acquainted with the use and the working of the McLeod gauge. An x-ray diffraction unit is also available but is primarily used by the staff.

Leeds University

The B.Sc. Special Physics Honours course embraces a certain number of experiments in vacuum technique scheduled for the second and third year. Post-graduate research* concentrates very largely on

'No special training in laboratory. Research students in low temperature physics are precipitated into vacuum work at a very early stage and usually manage very well. I think a single experiment on vacuum techniques during the undergraduate course is probably desirable but a formal course in the subject I regard, after trying it in a minor way, to be rather a waste of time. The average good honours man can pick up the practical parts very rapidly but for the rather less academically inclined and less able students generally I can see that a good course in vacuum techniques might be useful. The one course I have seen struck me as trivial.'

low-temperature physics and this, of course, incurs considerable handling of vacuum apparatus.

Leeds College of Technology

In the Department of Electrical Engineering and Physics, courses are provided in vacuum technology for part-time day students undertaking the Ordinary and the Higher National Certificate in Applied Physics. Parallel courses, *i.e.* an elementary and an advanced course, are available for general enrolment to students with the requisite background in science and mathematics. The courses cover theory and provide for demonstrations and practical work.

Liverpool College of Technology

Vacuum practice is dealt with in the part-time course for the Graduateship of the Institute of Physics and the courses in Applied Physics. In the Chemistry Department, research is conducted on the absorption of gases at low pressures.

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London University

All colleges of London University provide some experimental vacuum work to be carried out by the student reading for the B.Sc. Special Honours Degree but the intensity of such training and the particular problems set for the student depend very largely on the individual interests of the lecturer in charge and vacuum apparatus is frequently used in experiments for purposes other than investigating problems related to vacuum physics itself. This applies in particular to Part 2 of the aforementioned course.

Training in vacuum practices begins, in earnest, only during post-graduate research. For example, *Birkbeck College*, *King's College*, *Queen Mary's College* and *University College* have large vacuum installations which are employed for research carried out in the various Science, Electrical and General Engineering Departments and on such subjects as atomic and nuclear physics in connection with the operation of particle accelerators. Further subjects are low-temperature physics, gas discharge phenomena, electron and ion optics, etc.

At the *Royal Holloway College*, research specialises in problems connected with vacuum metallising and the preparation of multiple layers for high reflection or anti-reflection purposes. A much used research tool is the electron microscope and in conjunction with its use vacuum replica techniques are practised. A total of 10 post-graduate students is permanently engaged in this type of research.

Finally, at the *Imperial College*, almost all aspects of vacuum engineering and its applications are practised. This latter college has an exceptionally wide variety of vacuum plant and equipment which is constantly employed by the Departments of Physics, Electrical Engineering, Chemistry, Chemical Technology and Instrument Technology. However, the apparatus is essentially reserved for proper research; there are no normal classes for vacuum physics and little research into the properties and performance of vacuum equipment itself is being conducted.

London Polytechnics and Technical Colleges

In some of the London polytechnics and technical colleges a more direct approach is made to formal training in matters pertaining to vacuum.

The *Northampton College of Advanced Technology** has a well-equipped vacuum laboratory where instruction is given to full-time (sandwich) students on the Diploma in Technology course and to engineering students who take physics as an ancillary subject. Special short courses and evening courses in vacuum technology are also arranged. The syllabus ranges from the production and measurement of reduced pressure to vacuum plumbing, leak-finding techniques, gas-solid phenomena, glass-to-metal seals and applications of vacuum technology in valve production, optical industry and metallurgy.

At the *Chelsea College of Science and Technology*, students preparing for the B.Sc. Special Physics degree measure pumping speeds, coat lenses with anti-reflection films and handle vacuum apparatus in connection with certain instruments, *e.g.* the Rayleigh refractometer.

Similar conditions prevail at *The Polytechnic, Regent Street*. Here projects in vacuum physics are undertaken by the student in Part 2, the final year

* See Poynton, F. Y., 'Training in Vacuum Technology', *Vacuum*, **1**, 92.

of the three-year Special Honours Degree course. Examples of such projects are the calibration of a Knudsen manometer for various gases, studies of the effects of gas-filling on the characteristics of Geiger-Müller tubes, the evaporation *in vacuo* of metals and dielectric materials, the study of molecular flow phenomena under unusual tubulation conditions and the pumping action of ionisation gauges. The emphasis in this work is on solving a problem associated with vacuum equipment rather than formal training in the use of the latter.

At the *Northern Polytechnic*, one of the two topics studied for Part 2 of the B.Sc. Special Physics Degree is 'Kinetic Theory and Discharges in Gases'. This course is more fundamental and mathematical in its approach than the normal technological courses. The relevant part of the syllabus includes gas flow and viscosity, thermal conduction, accommodation coefficients, radiometer forces, thermal molecular pressure, mechanism of diffusion pumps, design of pumping systems, and molecular beams. In an M.Sc. course on 'Electrical Discharges in Gases' considerable attention is given to related low-pressure physics. Furthermore, new courses leading to the Diploma in Technology and to the Graduateship of the Institute of Physics include vacuum techniques as part of the basic training.

At *Woolwich Polytechnic*, one of the two subjects taken for Part 2 of the B.Sc. Special Degree in Physics is 'Kinetic Theory of Gases and Vacuum Techniques'. This course is conducted at a high level from both the mathematical and experimental point of view. As part of the experimental projects undertaken for Part 2, the student usually has to design and assemble a high vacuum system, *e.g.* for use with an electron diffraction camera.

At the *Borough Polytechnic*, students following the course for Graduateship of the Institute of Physics experiment with gauges, pumps, Geiger-Müller counter tubes, and vacuum coating plant, practising calibration, speed measurement, filling techniques and deposition procedures respectively. The Department of Electrical Engineering and Physics also undertakes research on Geiger tubes, corona stabiliser tubes and other gas-filled electronic devices.

Loughborough College of Technology

An introduction to vacuum practice is provided in the Physics courses for chemists and chemical engineers.

Manchester University

Honours students in physics undertake a short laboratory course in the Department of Electrotechnics, which has a special vacuum laboratory. In the third (final) year of the course, students attend lectures on experimental physics which include two or three lectures on the theory and practice of vacuum technique. Several experiments in the third year require the operation of vacuum plant. In the Electrical Engineering Laboratories, a course in High Vacuum Practice has been run since 1958 for Honours students in Electrical Engineering. This consists of about 30 lectures covering kinetic theory, the production of vacua and measurement of low pressures. Joined to this is a laboratory course.

A great deal of vacuum apparatus is used in post-graduate research conducted in the departments of science and engineering.

Manchester College of Science and Technology

There is no special vacuum laboratory in the Physics Department and no experiments are conducted on the characteristics of vacuum equipment itself as such. In the third year of the full-time Physics course, however, some of the experiments involve the use of vacuum apparatus and the students learn about the performance of the various pumps and gauges, and become acquainted with the practical problems inherent in setting up small-scale vacuum systems.

University College of North Staffordshire

The Honours degree course in Physics devotes some time to vacuum physics. The respective programme is as follows: (*1*) A course of lectures on the kinetic theory of gases which includes the behaviour of gases at low pressures, (*2*) a series of 7-8 lectures on vacuum physics in the last year, (*3*) practical work involving vacuum techniques in the last two years,

Vacuum in Training the Undergraduate IV.

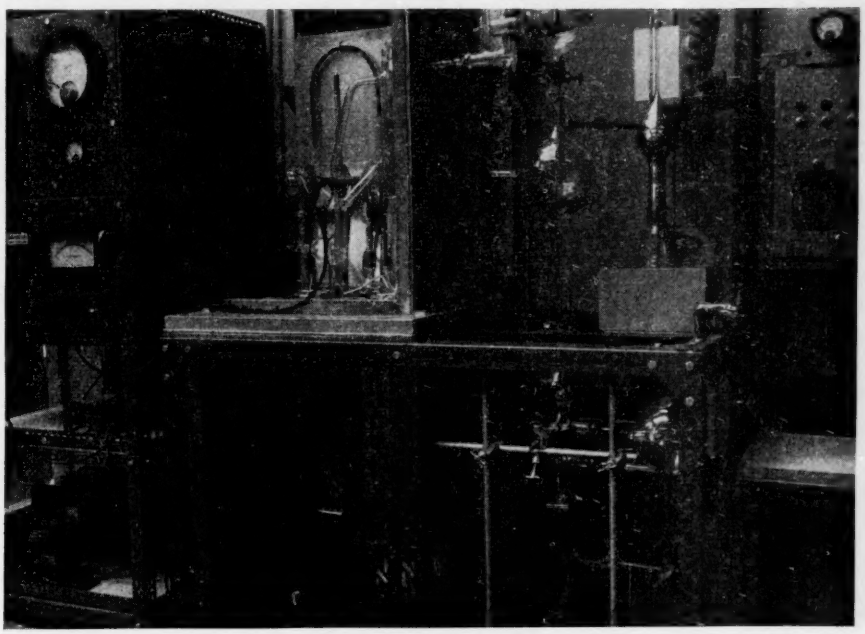

Fig. 4 Experiment on the calibration of an ultra-high vacuum gauge of the Bayard-Alpert type. Note the arrangement of bulbs and taps to permit gas at pressure of about 10^{-5} mm. Hg (recorded by McLeod gauge) to be expanded by a known ratio of about 100:1 on admittance to ionisation gauge.

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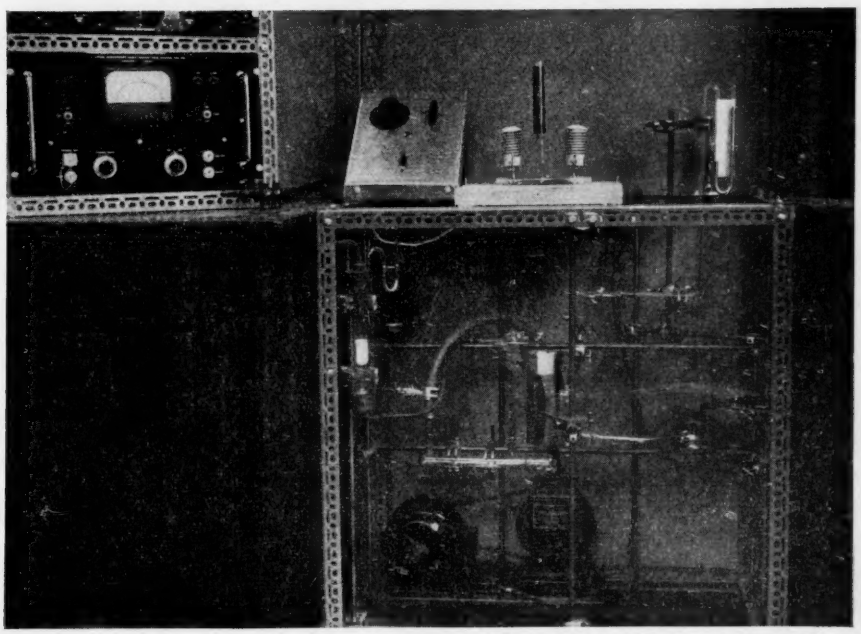

Fig. 5 Vacuum apparatus for investigation of the nature of gas-filling on the characteristics of Geiger-Müller counter tubes.

The above Figures illustrate vacuum apparatus used in experimental projects undertaken by students for Part 2 of the B.Sc. Special Physics Degree at The Polytechnic, Regent Street.

and (*4*) special vacuum physics problems as encountered in studies of the electrical breakdown of gases, thermionic and field emission etc.

Many of the research activities in the Department involve the exploration of vacuum physics proper. Post-graduate lectures and colloquia on advances made in this speciality take place from time to time.

Nottingham University

In the Honours Physics course a few lectures are devoted to the theory and use of pumps and gauges. Practical applications such as vacuum coating are also mentioned. One vacuum experiment is scheduled in the laboratory course and is essentially designed to give the student some preliminary experience with a rotary/diffusion pump system.

Nottingham and District Technical College

A course on Vacuum Technology has been arranged for evening students, but is not a regular feature of the programme. This course extends over two terms (about 24 weeks) and consists of lectures and laboratory work. Fifteen experiments are undertaken covering the production, measurement and application of low pressures. Among these experiments, the following are noteworthy as being different from the usual programme: Construction and calibration of a metal bellows manometer; measurement of the pumping speed of a diffusion pump for different gases; investigation of the degassing of glass and metal systems; degassing by various heating methods.

Low-pressure phenomena are discussed in lectures forming part of a Physics course complementary to the B.Sc. Special (Honours) Degree in Chemistry and it is planned to introduce a similar lecture programme in the 4th year for the benefit of students engaged on a sandwich training scheme in Electrical and Mechanical Engineering.

Oxford University

The Physics Department (Clarendon Laboratory) is the main centre of activities relating to vacuum practices. Students have the opportunity of conducting six experiments involving high vacuum apparatus. Vacuum techniques are also employed in nearly all branches of the extensive research work, which essentially concentrates on nuclear and low temperature physics. Six members of the technical staff out of a total of 60 are directly concerned with the high vacuum equipment. Trainee laboratory assistants receive practical instruction from these senior specialists on the staff.

Paisley Technical College

Instruction on high vacuum technique is given to part-time students preparing for the Higher National Certificate Course in Applied Physics and also to students reading for the B.Sc. Special Physics and B.Sc. Special Chemistry Degrees. The equipment includes a small oil diffusion and rotary pump, Pirani, Philips and McLeod gauges.

Reading University

Three or four lectures on the basic principles of vacuum technique are given to undergraduates in the final year in the Honours Physics course. Lack of time precludes the scheduling of more than one vacuum experiment in the laboratory course.

Demountable vacuum systems, including ultra-high vacuum systems (utilising ion pumps) are extensively employed in post-graduate research. Formal instruction in vacuum technique is regarded as unnecessary at the post-graduate stage.

Rotherham College of Technology

Three types of courses in High Vacuum practice are arranged in the Department of Electrical Engineering and Physics: (*a*) A course of $2\frac{1}{2}$ hours per week extending over approximately 32 weeks and forming part of the training for the Higher National Certificate in Applied Physics. This course is also attended by physics graduates who are specially interested in high vacuum, (*b*) special courses as, and if, required by the local industry, and (*c*) short courses extending over the whole day but not exceeding one week. The syllabus covers the theory and practice of the production and measurement of

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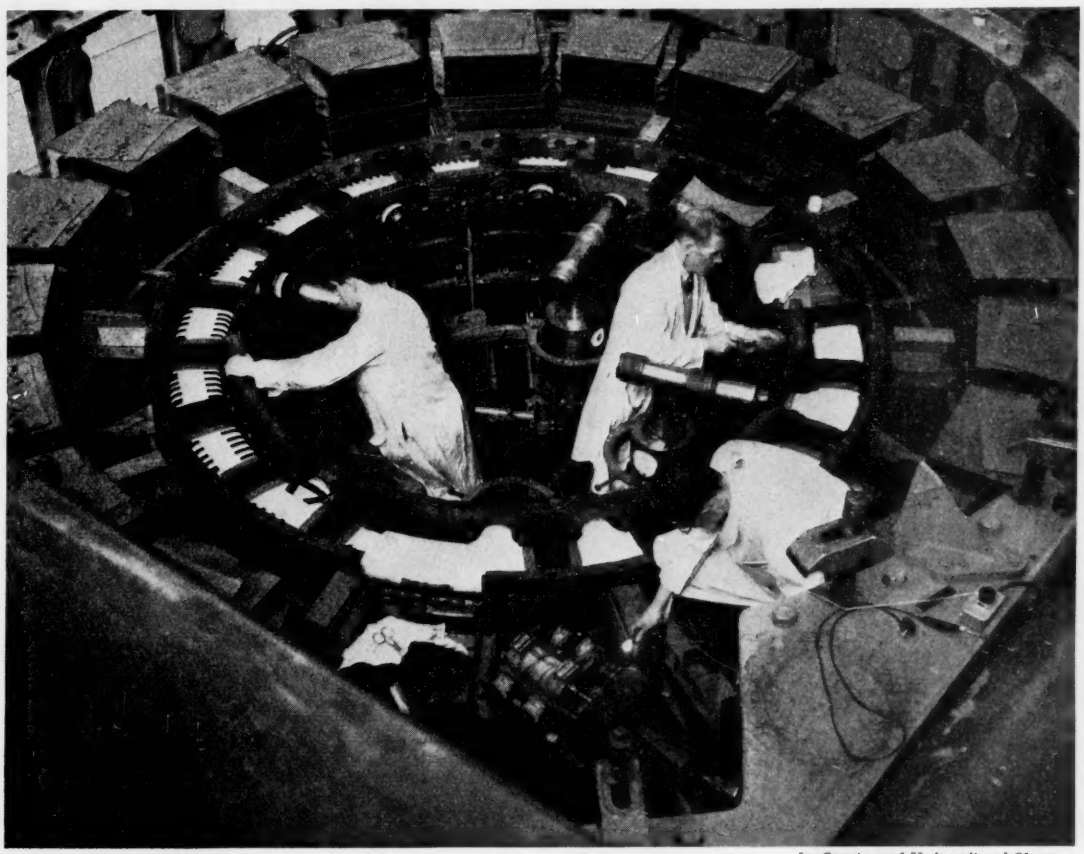
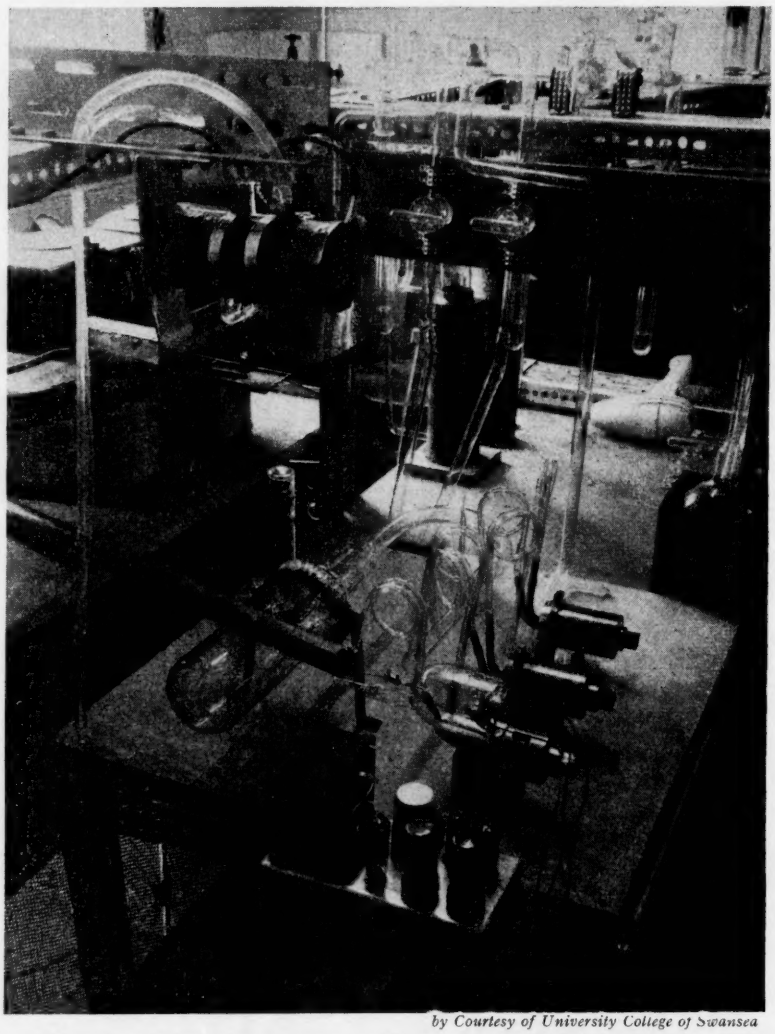
Vacuum in Post-Graduate Research I.



by Courtesy of University of Glasgow

Fig. 6 The synchrotron at the University of Glasgow. The upper pole of the magnet has been removed to show the ceramic donut. The sectors are sealed by Neoprene bands and evacuated at four pumping stations. The cold traps and compensating tombac connectors can be seen. The pumps are guarded by pneumatically operated valves directed by Pirani gauges.

Vacuum in Post-Graduate Research II.



by Courtesy of University College of Swansea

Fig. 7 Ultra-high vacuum system used in Department of Physics. Residual gas pressures of 10^{-10} mm. Hg. are obtainable in the ionisation chamber. In the foreground is shown the ionisation gauge and pump with its attendant power supply and a screened lead leading from the gauge to an electrometer. Behind and below the ionisation gauge are three all-metal greaseless valves. The valves, gauge and ionisation chamber are mounted on an asbestos table, and an oven (not shown) can be lowered over the system for degassing purposes.

vacua, kinetic theory and molecular and viscous flow phenomena, vacuum plumbing, leak detection, gas-solid phenomena, getters and certain applications. In addition, there is experimental work on most of these topics. In the full-time, one-week course, 2 hours of lectures and 4 hours of practical work are scheduled for each day.

St. Andrews University
Dundee

One fairly elaborate experiment is undertaken by Honours Degree students in Physics. Vacuum techniques are employed in the post-graduate work devoted basically to cryogenic and solid-state research. The departmental workshop is very well equipped and facilitates the assembly of a variety of vacuum systems and apparatus, including large glass and metal Dewar vessels.

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The Royal Technical College
Salford

Vacuum engineering forms part of the third year of the course for the National Certificate in Applied Physics and is included also in the full-time (sandwich) course on the same subject. The syllabus covers the production and measurement of vacua and touches also on the applications of vacuum in valve manufacture.

University of Southampton

Experiments of a vacuum engineering nature are only scheduled in the Physics Department. Both Special Honours and General Honours students conduct two experiments, one on the measurement of pumping speed and the other on the evaporation of aluminium. The lecture course includes two or three lectures on high vacuum technique.

Some vacuum apparatus is used in post-graduate research, but the Department tends to specialise in fields not demanding the attainment of low pressures.

Sunderland Technical College

Lectures and laboratory work on high vacuum technology are included in the Ordinary and the Higher National Certificate courses in Applied Physics. The final year of the Higher National Certificate (part-time) course provides a comprehensive programme in vacuum technology extending over 15 weeks.

Swansea University College

In the final year of the Honours degree course in physics, students attend 6 or 7 lectures on the fundamentals of vacuum practice with special emphasis on recent developments. Experiments are conducted on the calibration of gauges and the measurement of sparking potentials in gases at low pressure. Research students in the Department of Physics have to be fully conversant with the construction and operation of systems in which pressures down to 10^{-10} mm. Hg are maintained and also techniques involving extremely pure gases and clean electrode surfaces are used. The chief subject of the research work carried out in this department is ionisation of gases.

Wolverhampton and Staffordshire College of Technology

Interest in vacuum physics has grown recently, in particular, in the Department of Applied Science. It is planned to train students in general vacuum work and also to include the relevant aspects of vacuum technique in courses in radiochemistry.

Discussion

The above survey demonstrates the same differences in approach to teaching vacuum practices as is found in other branches of science between universities and technical colleges.

In university education the emphasis is on fundamentals, on training the student to think for himself, to read the literature, to construct and use apparatus for solving a problem. Where lectures and tutorials are concerned the teaching primarily concentrates on the more recondite and especially theoretical aspects of the subject. Furthermore, in an Honours Physics course, an inculcation of an understanding of the structure of science is considered

more important than the study of technology.

In technical colleges, on the other hand, the lectures are often more concerned with practical procedures and attempts at conveying details of the technology as required by a person working in industry. But this is not invariably so; for instance, in the case where the student prepares for the B.Sc., there is little distinction between the university and technical college approach except that the technical college students have to attend more lectures.

However, this difference of approach can be expected to be more marked in the future as courses for the Diploma in Technology become established at the technical colleges. To quote an example, take semiconductors. A course on semiconductors at the university will present the subject in its relation to solid-state physics, whereas lectures at the technical college may well concentrate on semiconductor elements and their applications in electronic circuits.

Generally speaking, this distinction is desirable and indeed should be promoted as there is undoubtedly room for both kinds of trained graduate in practical life. But looking at the situation more closely, there are aspects of the present vacuum training methods where changes could usefully be introduced.

Let us consider first the conditions at the university. It is frequently the case that a three-year full-time course for an Honours Degree in Physics provides a number of experiments relying on vacuum as an essential tool but only one of them is devoted to an exploration of the performance characteristics of the vacuum plant itself. All further practical experience resulting from the manipulation of vacuum apparatus would, as the undergraduate is bound to realise, be postponed until he joins post-graduate research. This may be satisfactory to the student who has decided to do so, but is it for the person who leaves the university after the first degree? In this connection it must be emphasised that a considerably larger number of graduates proceed to the Ph.D. in the U.S.A. than in this country.

It is admitted that the syllabus for the Honours Degrees in Science and Engineering are already very crowded and this condition may worsen as knowledge advances but, in spite of this, the author believes that the time has arrived for some revision of undergraduate training in experimental physics. For instance, take a laboratory course on the properties of matter. It can often be found that considerable time is spent in the first year of a degree course on the various methods which exist for the measurement of elastic moduli, surface tension and gravitational acceleration. Would it not be preferable from the student's point of view to carry out one well-planned experiment on each of these topics instead of being required, to measure the surface tension of water, *e.g.* in, say, four or five different ways? The time thus saved could be employed for more experimental work on vacuum apparatus.

There is no reason why lectures and/or experiments on vacuum apparatus should be considered to be of a trivial nature or should lack interest in fundamental concepts. Indeed, a properly planned experiment aimed at the exploration of vacuum apparatus characteristics can be far more attractive to the student than many of the present-day routine laboratory exercises and surely one of the aims of any science course is to excite and intrigue the novice. A discourse on the distinction between vapour pumps of the diffusion and ejector type, for instance, (often not shown at all in the syllabuses available), could be readily related to important phenomena in the field of the kinetic theory of gases. The provision of gas-ballast devices on rotary pumps would serve as an excellent example for the difference in behaviour of permanent gases and vapours; the mathematics involved could be readily appreciated by any undergraduate. Finally, instruction on the working principle of the Roots pump, contrasted with that of the normal rotary pump, would provide an excellent opportunity for the application of pressure-volume diagrams of gases.

Now turning to the vacuum training programmes provided by technical colleges we seem to notice a trend in the opposite direction, *i.e.* a certain over-emphasis of purely technical matters. Quite an appreciable number of syllabuses received by the author in the course of this enquiry make special mention of lectures on 'vacuum plumbing' and

'greases, waxes and cements used in vacuum work'. Surely much of the information presented in these lectures on gadgets and properties of ancillary construction materials can be obtained without difficulty by the student, direct from technical books which are easily available or manufacturers' catalogues, and the lecture time could be spent more profitably on information less readily accessible.

Similar criticism appears justified in connection with the laboratory work scheduled in vacuum courses of technical colleges. The straightforward calibration of, say, a commercial Pirani gauge against a McLeod gauge is little more than a routine exercise, essentially necessitating the taking of readings only. Appreciably greater benefits could be obtained by making the practical work more problematical. The fabrication of a hot-wire gauge in a rigged-up bridge circuit is of incomparably higher educational value than the handling of the finished, commercially available, instrument and at the same time offers the opportunity of exploring the relationship between wire temperature and gauge sensitivity as determined by thermal conduction and radiation effects.

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This discussion will have indicated to the reader the line on which, in the opinion of the author, vacuum training could be organised more satisfactorily. It lies somewhere between the provisions made for vacuum training in the ordinary Honours Physics course at the University and the syllabus of the special course normally provided at technical colleges. As it is, the former is not sufficiently detailed to be expected to convey the proper 'feel' for vacuum plant characteristics to the student, whereas the latter appears to be somewhat excessively preoccupied with technological detail at the expense of such matter as would bring the student's critical faculties into play effectively.

The present enquiry is not claimed to be exhaustive with regard to vacuum training facilities available to chemical engineers and metallurgists. However, the impression prevails that education in these spheres lags considerably behind the present state of progress of vacuum engineering in industry. This may be the inevitable result of the high cost of the equipment in question but one would think that at least one of our major colleges should contemplate the introduction of training courses and research programmes on modern vacuum technology and its applications so that more fundamental work of an academic nature could be initiated.

The point is often made that the design of modern vacuum apparatus for industrial purposes tends to become more and more accomplished. Indeed, there is vacuum plant in existence which operates almost fully automatically. This development is greatly appreciated but should not obscure the issue. The real beneficiary is the plant operator who needs no longer to have a full understanding of vacuum practices. But the graduate who has chosen an industrial career should be enabled by his professional education to act expertly when considering the advantages, or otherwise, of vacuum processes, and designing vacuum apparatus adequate for the purpose. Above all, he should have a sufficient understanding of all the fundamentals in order to plan successfully any research programme which calls for the use of vacuum plant.

A full understanding of vacuum technology in all its aspects and a possible participation in the development of that science is no longer a matter of being familiar with some selected elementary physical phenomena and a few apparatus designed for their practical application. To prove this, one needs only remember the multitude of major innovations made recently in the field of vacuum practice. Briefly these are, the gas-ballast pump, the Roots pump, the introduction of low-vapour pressure pump fluids, the latest developments in ionisation gauges, the alphatron, the omegatron, various leak-testing procedures, ultra-high vacuum techniques, the construction of plant for experimental nuclear physics and the rapid advances in vacuum metallurgy.

There is no suggestion of deprecating the excellent results of the development and research activities of British vacuum equipment manufacturers, if, at the end of this survey we ask ourselves the question: Is it not true to say that the pioneer work leading to major developments of the kind just mentioned has not often enough begun in this country? It is admitted that the origin of principal advances is fre-

quently determined by the genius of a particular man such as Gaede in Germany or Langmuir in the U.S.A. But are we satisfied that everything possible is done at our universities and technical colleges to put experts in the field, sufficiently conversant with the fundamentals of the art to share in its future progress ?

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SOME VACUUM PROBLEMS IN THE VALVE INDUSTRY

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Summary

THE END OF LIFE in a valve is regarded as being due to deterioration of the cathode through the poisoning action of some residual gases. This paper deals with some problems encountered in the valve industry in reducing the residual gases to a minimum. Simple considerations show that the gas on the surfaces of the assembly and the glass envelope may be many times that in the space. The surface gases may be due to gas adsorbed from the atmosphere or to contamination during manufacture. Meticulous control of the material used in the valve by chemical analysis before fabrication helps to reduce one form of contamination and clean rooms and filtered air conditioning help in reducing contamination during the assembly. The valve engineer attempts to eliminate residual gases by suitable heat treatment and processing during pumping. The mass spectrometer is proving a useful tool in detecting contaminants in residual gases. New trends in vacuum technology show that all-metal pump systems with metal taps are tending to replace glass systems and greased taps when single valves are pumped. The improved form of ionisation gauge, which can be used as a pump as well as a measuring device is being used to continue pumping after removal of the main tube from the normal pumping system. The ionisation gauge can also be used as a sensing device for control of automatic pumping systems. Cathodes are still the subject of intensive development and while special cathodes have been introduced for particular valves, the oxide cathode remains supreme in receiver valves. New methods of control have resulted in denser and more uniform cathode coatings on mass production tubes. In research, the ability to reach pressures of less than 10^{-10} mm. Hg has resulted in the detection of gases desorbed from various metals at relatively low temperatures. Some of the gases have a poisoning effect on oxide cathodes.

Sommaire

ON CONSIDÈRE LA FIN de la vie d'une valve comme étant due à la détérioration de la cathode empoisonnée par les gaz résiduels. Cet article traite des problèmes rencontrés dans l'industrie des tubes, pour éliminer le plus possible les gaz résiduels. De simples considérations montrent que la quantité de gaz se trouvant sur la surface interne de l'enveloppe de verre, sur les électrodes et l'assemblage est bien plus grande que la quantité de gaz restant dans l'espace interne, après pompage. Ces gaz peuvent être des gaz adsorbés de l'atmosphère ou dûs à la contamination pendant la fabrication. Un controle méticuleux des matériaux employés, par analyse chimique, permet de reduire une partie de la contamination qui sera plus tard largement réduite si le montage se fait dans des ateliers propres, alimentés en air filtre. Pendant le pompage, différants procédés comme le chauffage des électrodes à haute température, etc. éliminent une grande partie des gaz résiduels. Des groupes de pompage entièrement métalliques remplacent de plus en plus les groupes en verre lorsque seulement un tube est pompé à la fois. Le spectromètre de masses est très éfficace dans la détection des contaminants contenus dans les gaz résiduels. Le jauge à ionisation améliorée peut pomper aussi bien que mesurer la pression, et est employée pour continuer le pompage après isolement du groupe de pompage. La jauge à ionisation peut aussi être employée comme dispositif de controle de groupes de pompage automatiques. Les cathodes sont encore l'objet de recherches poussées, et tandis que des cathodes spéciales ont étè fabriquées pour certain tubes, la cathode à oxyde reste encore la plus employée dans les tubes de réception. De nouvelles méthodes de fabrication ont permis de obtenir des revêtements de cathode plus denses et plus uniformes en production de masse. Dans la recherche, il est possible d'obtenir des pressions moindres que 10^{-10} mm. Hg ce qui permis de détecter des gaz provenant de différents métaux, à des temperatures relativement basses. Quelques uns de ces gaz empoisonnent les cathodes à oxydes.

INTRODUCTION

An electronic valve is a device in which electrons are made to perform operations under the action of electric and magnetic fields. Although the transistor can be regarded as a valve in this definition, consideration is only given to valves in which the electrons operate under vacuum conditions. The word 'vacuum' in the valve industry is much abused and has a very indefinite meaning. In order that a valve should work, the electrons must be able to perform their allotted motions without colliding with gas molecules, which implies that their mean free path must be greater than the distance between electrodes. In Table I are given some maximum electron path lengths in various classes of valves, and also the gas pressures which must be attained to give

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them these mean free paths. It is seen that only in the C.R.T. and T.W.T. (Travelling Wave Tube) is the path length more than a few millimetres and the pressure required in the case of the C.R.T. is only 4.7×10^{-5} mm. Hg, whereas if we take the case of the subminiature valve with a path length of say 100 microns then the pressure to which the valve need be pumped is only about 0.14 mm. Hg. In normal valve production these pressures are easily attained.

That the mean free path should be large is less important than the other requirement of a minimum residual gas for long life. Most valves have oxide cathodes in one form or another and it has been shown that oxygen[1], carbon monoxide and chlorine and water vapour have a poisoning effect, so that it is important to eliminate these gases from the system.

Table II shows the rate at which molecules of gas bombard each square centimetre of surface at various pressures.

If we assume that an impinging molecule of gas must strike a target the size of 3 Å in order to be adsorbed on the surface of an oxide cathode and have a chance to react chemically with the free barium, and further that the number of barium atoms on 1 sq. cm. of cathode surface is approximately 10^{15}, then the table shows that at pressures of 10^{-5} mm. Hg and greater, there is a chance that a residual molecule bombards a barium atom about once per second.

At a pressure of 10^{-7} mm. Hg the rate of bombardment is reduced and it takes 27 seconds before the whole of the surface is hit whereas at 10^{-9} mm. Hg it would take about 45 minutes. These figures suggest that there is the possibility of very rapid poisoning of an oxide cathode by residual gases but the position is mitigated by three main factors:—

(*1*) Not all the residual gases are poisonous so that in a total pressure of 10^{-5} mm. Hg the partial pressure of poisoning gas may be quite small.

(*2*) There is only a small probability that a molecule impinging on the cathode surface will be adsorbed even though it comes into close proximity with the barium atoms.

(*3*) The barium atoms are continually replenished by chemical action between the oxide and the base metal.

It may be calculated[2] that if every barium atom in an average cathode is responsible for electron emission then the life should be of the order of 100,000 hours. The failure to reach full service life is attributed to the action of residual gases gradually reducing the cathode emission.

The valve engineer's problem is twofold. He has (a) to design the assembly so that it performs the required function of amplifier, oscillator, etc., and (b) to eliminate gases from the working space in the valve envelope in order to facilitate proper operation and to ensure adequate service life of the valve.

Table I. **Pressures at which Electron Mean Free Paths are Equal to Actual Electron Paths in Typical Tubes**

Tube Type	*Maximum Distance Travelled By Electron mm.*	*Pressure for Mean Free Path of This Distance mm. Hg*
Subminiature Valve	0.2	1.4×10^{-1}
Receiver Valve	2	1.4×10^{-2}
T.W.T.	200	1.4×10^{-4}
C.R.T.	600	4.7×10^{-5}

SOURCES OF GAS IN VALVES

The gas remaining in the free space of a valve is a very small proportion of the gas attached to the surfaces in the adsorbed state, and possibly present in the interior of the solids forming the valve

Table II. **Molecular Bombardment Rates at Different Gas Pressures**

Gas Pressures mm. Hg	10^{-1}	10^{-3}	10^{-5}
Bombardment Rate $cm^{-2}\ ^{-1}$ sec.	3.5×10^{19}	3.5×10^{17}	3.5×10^{15}
Gas Pressures mm. Hg	10^{-7}	10^{-9}	10^{-11}
Bombardment Rate $cm^{-2}\ ^{-1}$ sec.	3.5×10^{13}	3.5×10^{11}	3.5×10^{9}

structure.

This can be shown by considering a typical receiving valve, the surface areas of which are shown in Table III. Again, we assume that the surfaces support 10^{15} molecules of gas per square cm. The table shows that at a pressure 10^{-3} mm. Hg the surfaces hold 1.7×10^{2} times more molecules than are present in the free space and as the pressure is decreased to 10^{-7} mm. Hg the number of molecules in the free space decreases also, but the number on the surface remains substantially constant and the ratio becomes 1.7×10^{6}.

These ratios may be reduced if the pressure is reduced because at low pressures the coverage of the surfaces will not be 100%. On the other hand, the effective area of surface may be many times that calculated. Some experiments on the coverage of residual gases on tungsten at a pressure of 10^{-9} mm. Hg show that it is only one part in 10^{6}; even so, it is seen from Table III that this still leaves 1.7×10^{2} times more molecules on the surface than in the free space. As can be seen, in these conditions the cathode and heater contributes about 1/12th of the total area and, in effect, this fraction may be considerably larger because of the rough nature of the surfaces. These surfaces when heated will give off the gas into the free space, generating a pressure which can be calculated on the basis of the kinetic theory to amount to 10^{-3} mm. Hg approximately, in a normal receiving valve. This pressure will not persist in the tube but will be reduced by the adsorption of the glass, by the action of getters and by the pumping action of the electron current (see page 35). On cooling, the cathode will re-absorb some gas from the glass walls. This is illustrated by measurements made on a hydrogen thyratron filled to a pressure of approximately 0.8 mm. Hg. The thyratron was run for about 300 hours keeping the hydrogen pressure constant. Subsequently the tube was exhausted while the cathode was cold and the various parts were heated individually. It was found that gas may be desorbed from all parts in the valve such as the glass walls, assembly, cathode and heaters, by far the greater part coming from the glass envelope and about 20% from the cathode.

The glass envelope may be considered to be one of the valve components, and in fact may present the largest single surface inside the valve. The mass spectrograph has been used in recent years[3] to examine the gases liberated from glass. The tests show that much water vapour is evolved on heating and, in addition, many glasses give off varying quantities of carbon monoxide, carbon dioxide, and other heavier molecules, as the temperature is increased to a value near that of the softening point.

Many of the heavier gases, apparently liberated from the glass, may be due to the dissociation of oil vapours from the diffusion pumps used to pump the mass spectrometer. Even when mercury vapour pumps are used oil vapours may be detected originating from the backing pump oil.

Another source of gas in glass is due to furnace

Table III. **Distribution of Gas Molecules in the Space and on the Surface in Leak EL41 of Tube**

		No. of Molecules at Pressures (in mm. Hg) of 10^{-3}	10^{-5}	10^{-7}	10^{-9}	10^{-11}
Volume of space in tube	13.9 c.c.	4.6×10^{14}	4.6×10^{12}	4.6×10^{10}	4.6×10^{8}	4.6×10^{6}
Area of glass	30.5 sq cm		3.05×10^{16}			
Area of inert parts, anode, grids, etc.	41.71 sq cm		4.17×10^{16}			
Area of cathode and heater	6.21 sq cm		0.621×10^{16}			
		Total	7.83×10^{16}			
(No. of Molecules on surface) / (No of Molecules in Space)		1.7×10^{2}	1.7×10^{4}	1.7×10^{6}	1.7×10^{8}	1.7×10^{10}

gases which are trapped during the process of melting, and glasses melted in electrically heated furnaces have been found to have a smaller gas content than those melted in solid fuel furnaces.

Exposure to atmosphere during long storage also causes increased water vapour content. The carbon dioxide in the atmosphere, together with water vapour, form a weak acid which etches the surface and increases the effective area, on which water vapour may be adsorbed.

A similar action may occur during glass working with flames if there is a large sulphur content in the gas used. The sulphur is oxidised to sulphur dioxide, which has a more vigorous action on the glass than carbon dioxide and may produce sodium compounds which, during valve processing, may reduce to metallic sodium. Normally, the sulphur content of town gas is maintained at a level at which this action is slight, but it is advisable to perform periodic checks on the quality of the gas.

The outgassing of glass has been the subject of investigations at the Dow Corning Glass Works[4]; confirming that water vapour was the main constituent evolved. The results can best be expressed in the form of an equation

$$V = m\ t^{\frac{1}{2}} + s$$

where V is the quantity of gas evolved, t is the time, m and s are constants. Thus, if the quantity is plotted against $t^{\frac{1}{2}}$, the result is a straight line, the intercept of which is s and the slope m. s represents the quantity of water vapour which is desorbed from the surface. It therefore depends upon the state of the surface and the previous history of the glass. It was found possible to reduce s by etching the surface with dilute hydrofluoric acid.

The constant m depends upon the diffusion coefficient of the gas through the glass, upon the temperatures, and upon the concentration of gas molecules in the glass. If these factors are known for a particular glass, it is possible to calculate the time required to reduce the gas content of that glass to any desired fraction of the original amount at any practical baking temperature.

Metals also have the property of retaining gases not only on the surface but also in the body of the metal. In the case of metals, water vapour is not one of the main occluded gases. These may vary according to the metal. For example, nickel desorbs carbon monoxide in relatively large quantities, and hydrogen to a lesser extent. As in the case of glass, most of the gas comes off within a few minutes of heating. There is also a slower diffusion out from the centre of the metal. Tungsten and molybdenum adsorb nitrogen and carbon monoxide, some of which can be desorbed at relatively low temperatures, as described in a later section.

Contamination of thoroughly outgassed metals when exposed to air is exceedingly rapid, and the whole effort of outgassing at high temperatures may be wasted if much time elapses between outgassing and usage. Outgassed components must be stored in vacuum chambers.

Also, metals may give off gas when bombarded with electrons, some of which may be gas which has been adsorbed on the surface, but, more probably, the bulk of the gas liberated in this manner originates from the reduction of metal oxides, which almost invariably cover large parts of the metal surfaces. The phenomenon can be observed when the potential on the anode of a diode is gradually increased from zero upwards. At approximately 6 Volts the emission falls due to the poisoning of the cathode by oxygen attributed to the dissociation of nickel oxide (or sometimes barium oxide) on the anode. In most cases the poisoning is only temporary. It has been shown[5] that the bombarding energy of the electrons is equal to the dissociation energy of the metal oxides.

ESTABLISHED MANUFACTURING TECHNIQUES

The first requirement of the valve engineer is that he should be assured of the quality of the materials used in the manufacture of his valves. For this purpose rigorous specifications are laid down for each material and a special department is set up in which analyses of the batch materials are made to make certain that the quality is maintained. It is

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the valve engineer's duty to employ techniques suitable for both reducing the gas content of glass and metals to a minimum and preventing contaminants of any kind from reaching the interior of the valves. Normal practices are degreasing of all components, washing the glass-ware and heating all metal parts in either vacuum or hydrogen. The task is extremely difficult for the valve engineer, since he very seldom has information on the previous history of the materials employed—particularly on the glass which may reach him in a partly weathered condition.

The prevention of foreign matter, such as dust, pieces of wool, fibre etc., entering the valve envelope is important, and nowadays the valve manufacturers tend to arrange for the assembly shops to be ventilated with filtered air maintained at a slightly higher pressure than the outside atmospheric pressure to prevent ingress of dust. The operators wear nylon overalls and caps, and the assembly parts are handled with nylon or plastic gloves. In many cases the assembly is welded by machines enclosed in glass-topped boxes, each box having an individual air supply and glove openings for the operator. A complete assembly unit designed for operation in a dust-free atmosphere for preventing dust, etc., will incorporate separate changing rooms with lockers for outdoor clothing, separate wash places, and toilets. In shops where pumping is carried out, the pumps will be placed outside the room. The walls, floor and ceiling are made of tiles or other glazed material and all doors and windows etc., are made flush with the walls to prevent accumulation of dust on ledges and cupboards, see Figs. 1a and 1b.

Pumping of the Valves

The basic tools available to the valve engineer for pumping tubes are oil-sealed rotary pumps and oil and mercury diffusion pumps. The use of the rotary pump for obtaining a rough (backing) vacuum is almost universal. There is a considerable difference of opinion on the use of oil as opposed to mercury diffusion pumps. The advocates of oil pumps consider that the ability to pump down to 10^{-6}—10^{-7} mm. Hg without a refrigerant outweighs the disadvantage of a small degree of oil contamination inherently present, whereas the advocates of mercury pumps claim that the contamination in a mercury system is negligible. However, it has been shown by Blears[3], using a mass spectrograph, that oil contamination from the rotary pump may diffuse into a system through a mercury diffusion pump, so that some contamination may be present in both types of vacuum system. Greased glass taps, almost universally used on production systems, may introduce contamination in both oil and mercury systems, so that for the case of ordinary pumping requirements there seems very little to choose between them.

Recently[6], however, there have been reports on pumping to very low pressures of, say, 10^{-10} mm. Hg using mercury diffusion pumps in conjunction with well-designed liquid air traps, and so there may be a trend to return to mercury pumps.

The pumping systems employed in production vary in complexity from types pumping single tubes to types where a large number are pumped and processed simultaneously. The latter may have a very high rate of output.

Longer life and better performance in valves is very often synonymous with higher vacuum. In the past, the major factor limiting development in this respect was the stoving temperature at which the valve could be baked, due to the use of glass for the envelope. For some high performance, ultra high frequency valves, there has been a tendency to resort to glasses such as the C14 or HL6X type of glass which can be baked at temperatures up to 600°C. Unfortunately, these glasses, which contain a high proportion of silica, become porous at elevated temperatures, and atmospheric gases leak in at a fast rate, preventing low pressures being reached in pumping. Measures to overcome this condition have led to an additional complexity in pumping arrangements. The tube and its oven are completely enclosed in a bell-jar where the space surrounding the equipment is separately evacuated to pressures of approximately 10^{-5} mm. Hg. The low external pressure reduces the rate of leakage through

Layout for Industrial Valve Production I.

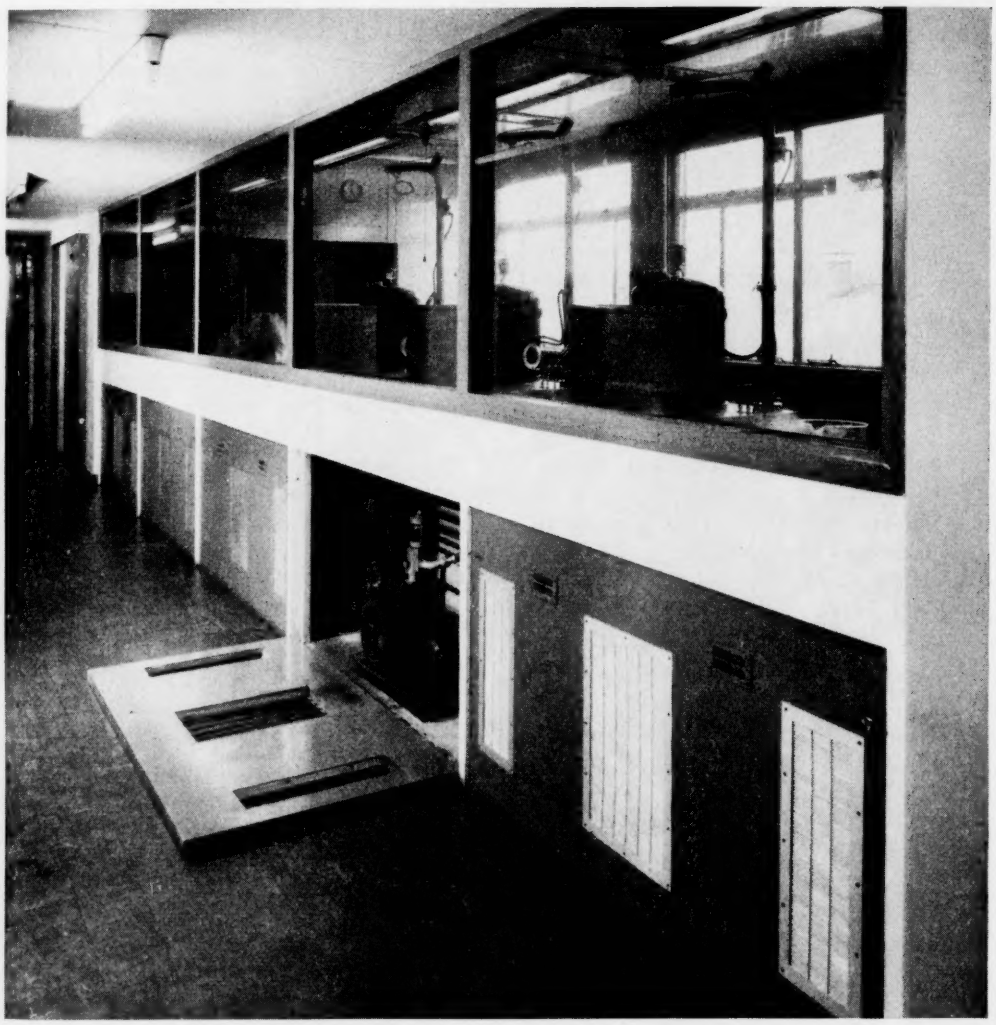

Fig. 1 (*a*). A typical clean room used for pumping photocells and image converters. The pumps are shown to be outside the room.

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Layout for Industrial Valve Production II.

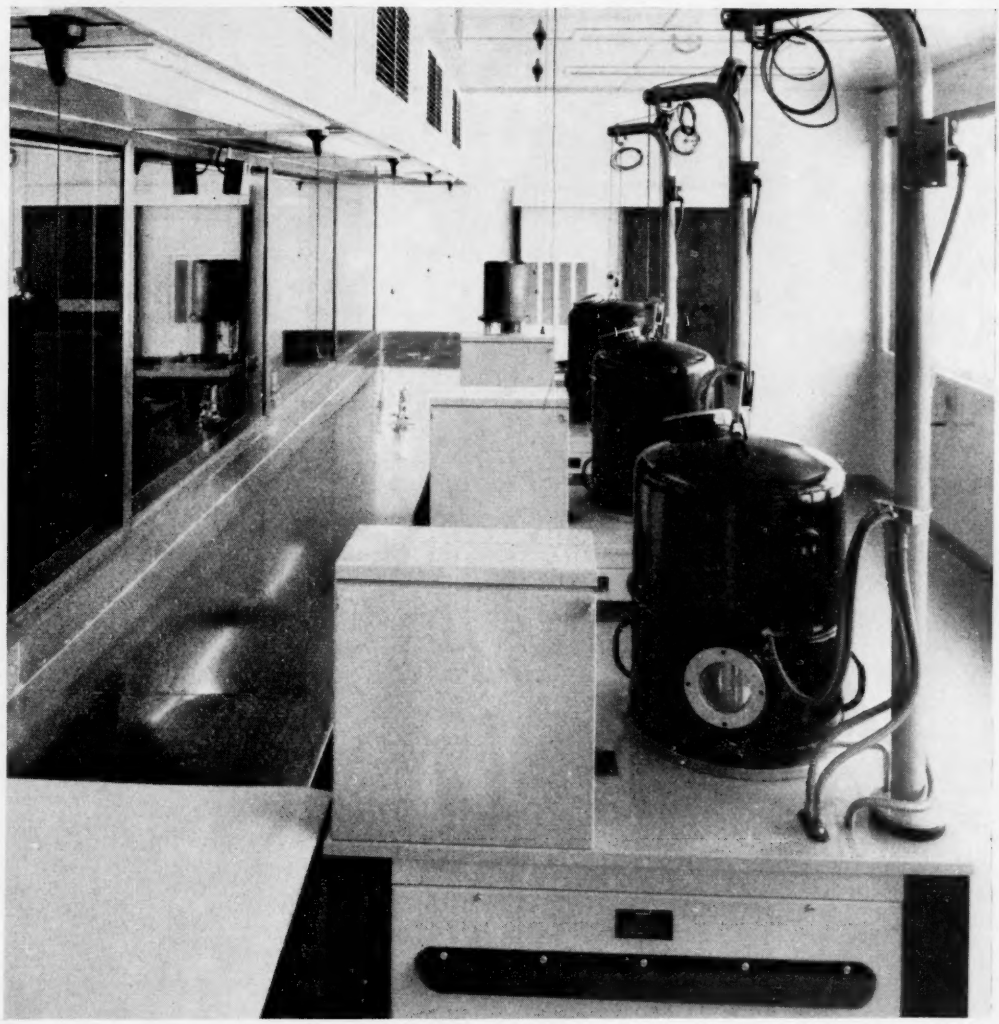

Fig. 1 (*b*). A typical clean room used for pumping photocells and image convertors. The air ducts for filtered air are shown on the upper right. All the walls and floor are tiled; the ceiling and the bench tops are metal. The pumps are under the bench with external access. The door in the background leads to changing rooms and toilets.

the hot glass and enables low pressures to be reached.

Disc seal valves also call for processing and pumping under a bell-jar.

The continuous efforts to produce higher and higher vacua with the attendant advantage of diminished contamination have led to the development of getter pumps[7], in which titanium is evaporated and deposited on the walls of the metal container. During the transit between the evaporating point and the walls of the vessel, gas molecules are attached to the titanium atoms and are carried to the walls; other molecules are adsorbed on the walls directly, so that the pressure of gas in the vessel is greatly reduced. The rare gas molecules are pumped by a separate gas discharge action in the same enclosure. Pressures of 10^{-9} mm. Hg are claimed for this pump but it has not been adapted yet for industrial use. One of the main practical difficulties is the cleaning of the pump after it has been opened to the atmosphere. For continuous pumping over several weeks, the getter pump may be very useful.

One of the most useful methods of pumping, introduced recently, for the more expensive and specialised ultra-high frequency tubes, is the provision of final pumping by means of an ionisation gauge. An ionisation gauge of the Bayard-Alpert type[8, 9] is connected to the tube to be pumped and the latter is removed from the manifold. The gauge is then run at electron currents of 10 to 20 mA and the pressure drops very markedly in the first few seconds after switching on and afterwards continues to fall, though at a reduced rate. Pressures of 10^{-10} mm. Hg have been obtained in this way after about two or three days' pumping. Finally the ionisation gauge is sealed off from the tube. The seal-off gases produce a pressure rise inside the tube but this is a transitory effect as the gases which are desorbed from the glass at the seal-off point are readily readsorbed by the glass on cooling[8].

Treatment of the Valves on the Pump

The treatment of tubes on the pump depends very largely on the purpose of the tube. In the case of valves embodying oxide cathodes the main procedure is common to all and can be briefly described.

The tube is first baked to remove surface contaminants, largely from the glass. The assembly is then heated by radio-frequency heating, to drive off the adsorbed gases from the various components. During this process, the glass is still warm from the previous baking and receives additional heat by radiation from the hot assembly. The operator continues heating until his pressure gauge shows that the desorbed gases have been pumped away. The oxide cathode is then heated at gradually increasing voltages for set periods in order to effect and complete activation. The final operation is to evaporate the getter.

The activation of the oxide cathode is one of the most important operations in valve manufacture, but in this context it is impossible to discuss any more than the general outlines of the process.

The mass spectrometer[10], has been used to analyse the gaseous products formed during activation. It shows that large quantities of carbon monoxide and carbon dioxide are given off together with the products of their decomposition, such as carbon, oxygen and a gas at mass 16 which may be methane. The volumes of the first named gases given off in the process are at a maximum value in the region of 1,200°K and result from the decomposition of the binder of the carbonates to oxides. Also, where activation of the cathode is in progress, large amounts of gases of the mass 2, 14 and 28 are liberated. These probably correspond to hydrogen and nitrogen. The volumes rapidly decrease during pumping, with the exception of the hydrogen volume which persists.

During activation and the drawing of current, the quantity of oxygen produced appears to be related to the value of the emission current. This indicates electrolytic liberation of oxygen. In practice, the activation of cathodes of a given type is expressed in terms of voltage applied to the heater for defined periods determined by temperature and pressure measurements, compiled during the development stages of the particular valve type. It is only the

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Plant for Industrial Valve Production I.

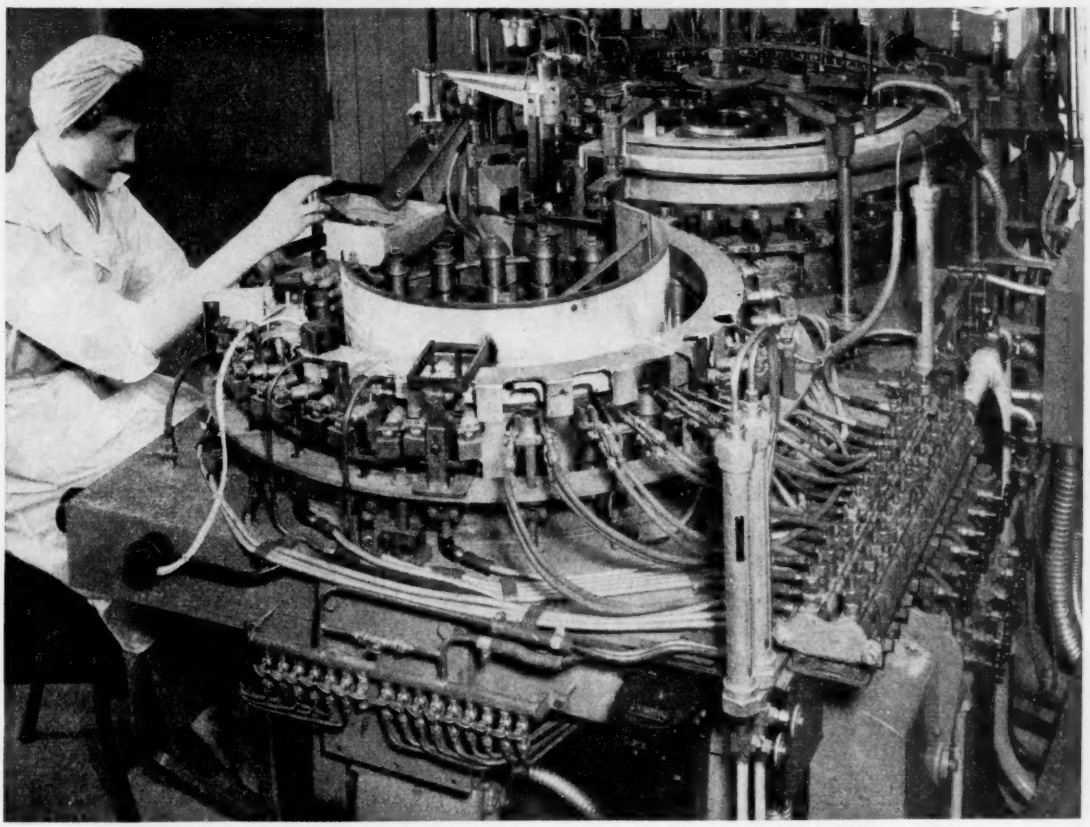

Fig. 2. Automatic pumping and sealing machine for minature valves.

meticulous control of the quality of the cathode nickel base, the particle shape and size of the carbonates, the outgassing of the assembly and the stability of the pumping rate which allows the valve engineer to specify the activity schedule leading to an uninterrupted production of millions of valves of the same type.

The procedure, as described above, is followed in the production of the majority of valves but those for special purposes such as transmitting valves, x-ray tubes, hydrogen thyratrons, and many others, are operated on the pumps under more exacting conditions than those which they will undergo in service.

In the case of tubes operating at high voltage, the operator is protected against x-rays by lead glass sheeting. Each operator carries a radiation detector which is examined periodically to ensure that the maximum radiation received does not exceed 0.3 R per week. The number of tubes which can be placed on one manifold for separate pumping is small and in many cases tubes are pumped singly.

For pumping and processing valves in the 'entertainment' group, mass production methods are adopted.

Plant for Industrial Valve Production II.

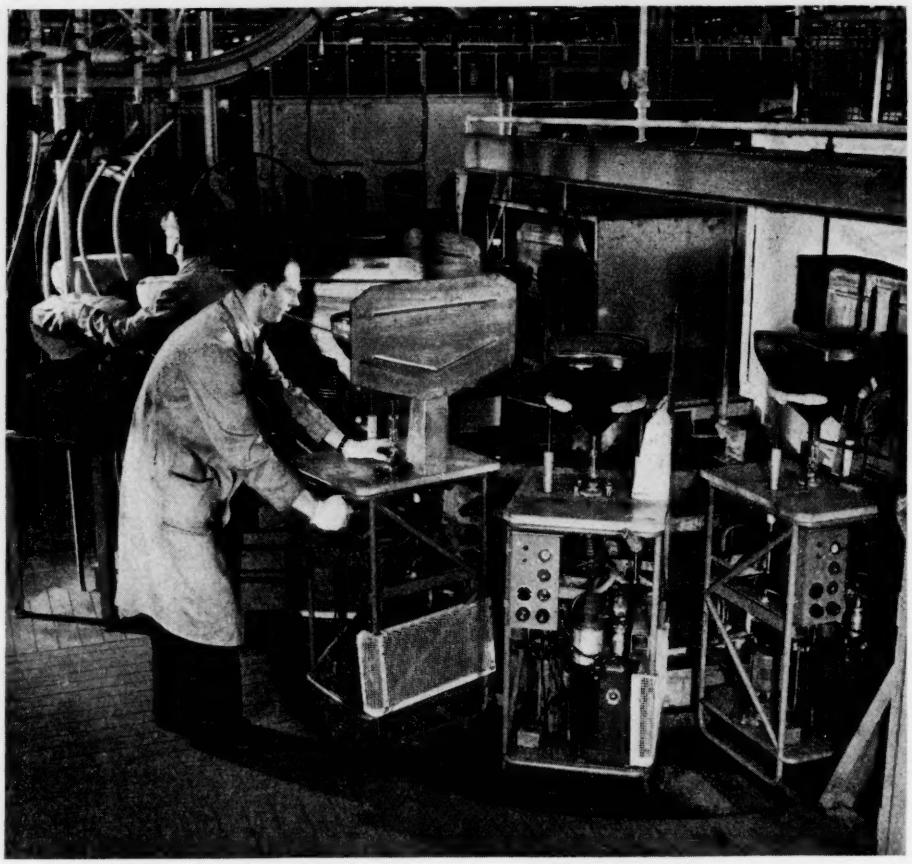

Fig. 3. An installation for pumping t.v. tubes.

The complexity of some of the machines used for automatic pumping and processing of entertainment and miniature valves is illustrated in Fig. 2. In general, the machines take the form of large circular tables with diffusion pumps fitted underneath, at equal intervals, to manifolds which protrude above the table. The manifolds terminate in rubber rings into which the valve stems can be pushed and which are self-sealing when the valve stem is removed. The diffusion pumps are backed by a large rotary pump or by a factory rough vacuum supply. The table revolves intermittently and the valves are carried through all the positions at which the processes required for each tube as described previously can be carried out in the established order. The final operation is to seal off the tube by flames and remove it from the machine. This machine requires only one operator who inserts and removes the tubes.

The rate at which these machines operate is determined by the size of the tube and the processing time, but outputs of upwards of 1,600 per hour are not unusual.

The same principles are employed for pumping and processing large television tubes, but because

of the size of the tubes the application is more complex.

Each tube is mounted on a self-contained pumping bench fitted with a rotary and a diffusion pump. A separate water pump circulates water through the cooling coils of the diffusion pump and through a car type radiator. The complete aggregate is mounted on a truck which moves on a circular track and carries the television tube through all the processing ovens, high frequency heating positions, etc., as in the case of the smaller tubes. A typical installation is shown in Fig. 3.

Pressure Measurement by Ionisation Gauges

In view of its importance to the practices described in this article it appears appropriate to insert here a brief note on the modern version of the ionisation gauge, developed by Bayard-Alpert[11]. The tube may be used as a gauge and as a pump. For pressure measurement, the electron current must be less than 100 μA; whereas for pumping, the electron current should be as high as possible. In a typical gauge, currents of 10—20 mA are used when pumping. On first switching on the gauge at high electron current, the pressure in the system falls within a few seconds to a comparatively low pressure. Thereafter the pressure continues to drop slowly over long periods. If p_1 denotes the pressure after the first rapid fall, and p_0 the initial pressure, then it can be shown that

$$\frac{p_0 - p_1}{p_1} = k\, i_e$$

where i_e is the electron current and k is a constant depending upon the gauge characteristics and the system to be pumped. This shows that, provided the electron current is kept small, it is possible to use the gauge for pressure measurement while its pumping action is negligible.

The calibration of a Bayard-Alpert gauge remains linear over a range of pressure from 10^{-4} mm. Hg to 10^{-11} mm. Hg,[9] but above 10^{-4} mm. Hg the sensitivity rises to a peak and then falls very rapidly in the 10^{-3}—10^{-2} mm. Hg region. The fall in sensitivity at high pressures is attributed to accumulation of ions near the collector, while the rise in sensitivity in the 10^{-3} mm. Hg region may be due to surface effects in the collector. The sensitivity of gauges available in the market ranges from 10—20 μA ion current per mA electron current per μ Hg pressure for nitrogen gas.

NEW TRENDS

All-Metal Pumping Systems

The valve engineer, like his colleague in other branches of engineering, is constantly seeking to improve the productivity of the existing manufacturing arrangements and, with this in view, he constantly watches the established pumping systems and methods with a critical eye.

For instance, higher vacua and increased freedom from contamination can be attained by using all-metal pumping systems with all-metal taps and all-metal connections for pipe unions incorporating metal gaskets. Metal systems are bakeable at high temperatures for cleaning and will probably be run at a temperature just below the permissible baking temperature of the valve itself.

Metal taps[9], connectors and gaskets[12], already available are illustrated in Figs. 4, 5 and 6.

Figs. 4 and 5 show two types of metal taps. Both employ the same principle first used by Alpert[9] of ramming a hard conical metal plunger into a soft copper orifice. The plunger makes its own seating. These taps have proved very robust and have been in constant daily use for several years.

A metal system can be bolted together using plane flanges on the individual units, between which is inserted a ring with two spring knife edges and two copper or aluminium washers. The depth of the groove between the knife edges, on the ring illustrated in Fig. 6, is adjusted so that there is just sufficient resilience to keep the knife edges pressed against the copper at all temperatures without the knife edges cutting through. Seals of this nature withstand repeated baking at temperatures up to 450°C., without adjustment and without leaking.

Such a metal system is pumped to, say, 10^{-7} mm.

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Hg by an oil diffusion pump, while the system is hot, and is then isolated from the pump by means of the metal tap. During cooling down, the system should be at a pressure of 10^{-8} mm. Hg or less. Pumping may be continued with an ionisation gauge until pressures of the order of 10^{-10}—10^{-11} mm. Hg are obtained.

Automatic Processing

Like other industries, the valve industry is interested in automation and it is searching for means to control the pumping of individual expensive tubes by sensing mechanisms which will control fully the pumping procedure according to the paritcular requirements of the tube. At present, each tube requires an operator for the adjustment of the baking time and temperature in accordance with the measured pressures, for outgassing the electrodes by radiofrequency heating, and activating the cathode at a rate also determined by the pressure developed in the tube. A great deal of the success of the production depends on the operator.

Some progress has been made with the idea of using the ion current from the ionisation gauge to initiate and control all these operations automatically, and at the same time guard the pumping system against accidents which could cause considerable damage to the plant with consequent loss of production.

A system such as this would reduce the number of operators required and lead to more uniformity in the output of tubes.

Glass as Envelope Material

The valve engineer's efforts towards improvements are continuously handicapped by the fact that glass is used for the envelope in the greater part of the valves. The gas content of glass is high and not easily reduced, and the relatively low softening temperature limits the temperature at which the assembly can be baked. The surface of the glass is subject to weathering effects during storage and may also contain cracks and small air bubbles. Glass is not strong mechanically, and is susceptible to thermal shocks. On the other hand, the low softening temperature of glass leads to easy manipulation, and the ability to adhere to metals makes it the obvious choice for valve making. The glasses available to the valve industry could be improved to a great extend by reducing the gas content.

It has been shown that much of the gas is introduced by the ingredients of the glass composition and much is also introduced by melting in gas or oil fed furnaces. The gas content may be reduced by using electrically heated furnaces and by degassing the constituents before mixing[13].

Glasses which soften at temperatures in the region of 800°C and at the same time remain impervious to atmospheric gases at high temperature, would be widely used if they were available.

Cathode Design and Fabrication

Development work on cathodes proceeds continuously, the aim being to produce a compact coating, mechanically strong and electronically conducting, which is easy to activate and which has a long life. The L-cathode, in which barium is distilled through a porous tungsten surface, has been thoroughly tested and appears to be excellent in tubes where there is heavy ion bombardment. Recent work [14, 15] has resulted in a cathode that may be used at the same running temperatures as the oxide cathode, with a correspondingly long life. However, expense and difficulties of manufacture will prevent its general use and the oxide cathodes are likely to remain by far the most numerous used in radio tubes.

In the field of oxide cathodes, the function of the base metal has been investigated.[16] The growth of electrically resistive films between the cathode material and the base metal in oxide cathodes has been shown to be due to the formation of barium silicates, and the substitution of silicon by tungsten of aluminium as reducing agents have led to the elimination of the resistive interface.

Research aimed at more highly conducting coatings, both electrically and thermally, has led to the incorporation of finely powdered nickel into the barium-strontium oxide mixture. Various percentages of nickel powder of closely controlled size are

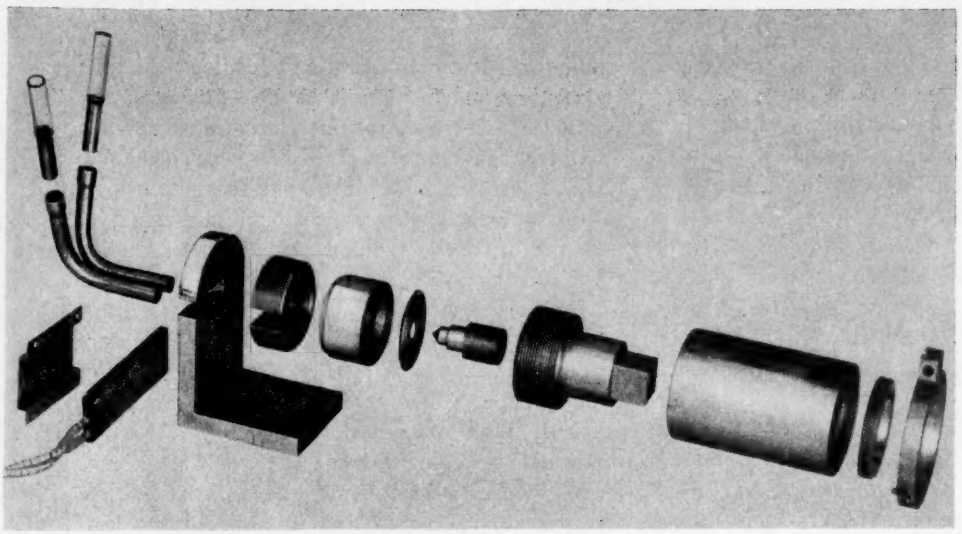

Fig. 4. Exploded view of the 6 mm. metallic tap. Open conductance—0.3 litres/sec. Closed conductance—10^{-10} litres/sec. Closing torque—40 ft.lbs. Baking temperature 450°C.

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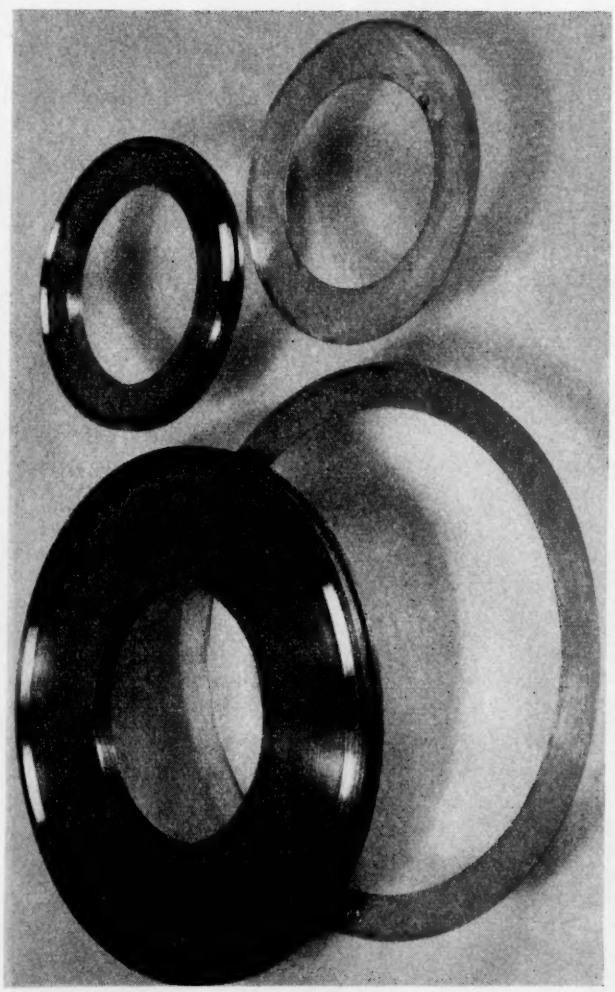
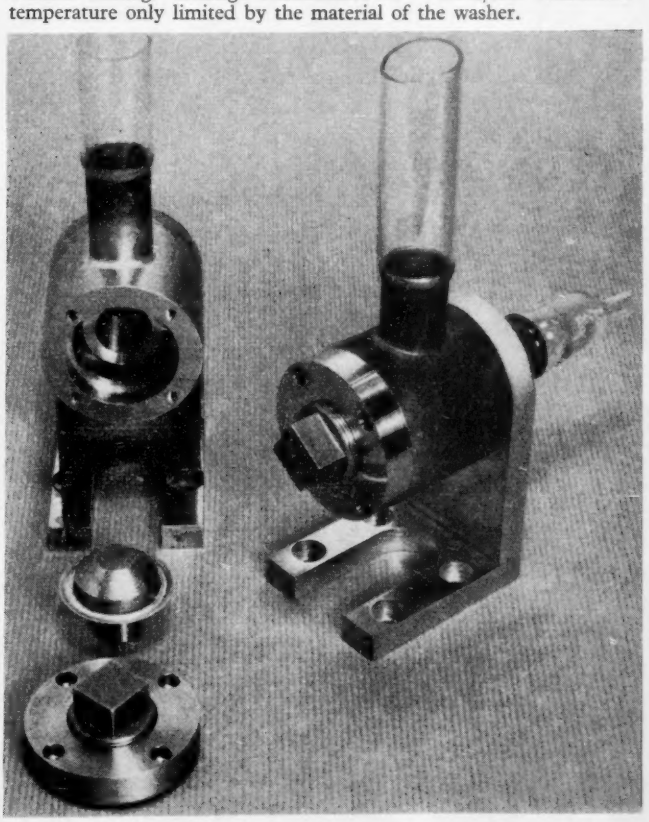


Fig. 5 (*below*). Completed 18 mm. bore tap on the right and component parts on the left. Open conductance—about 3 litres/sec., closed conductances—10^{-10} litres/sec. to zero. Closing torque—minimum 20 ft. lbs. Baking temperature—450°C.

Fig. 6. Sealing rings and washers. Two washers are used with each sealing ring. The groove between the knife edges is adjusted to give the necessary pressure on the washers at all temperatures without cutting. Leakage conductance 10^{-16} litres/sec. Maximum temperature only limited by the material of the washer.



included in the cathode according to the particular duties for which the cathode is intended and various processing schedules are applied to bring about the required coagulation of nickel and oxides.

New methods of precipitation of the carbonates have led to greater uniformity in size and shape of the carbonate particles. The desired particle size varies according to the purpose of the cathode, whether it is to be used in a receiving valve or in a pulsed tube, but sizes of the order of 6—12 micron are not unusual. Cathodes of barium strontium oxides are favoured for high slope valves, long life, and for high cathode temperatures. Triple oxides, including calcium oxide, have been found to be more resistant to poisoning when the cathode is run at a low temperature. The triple oxide cathode is also used for tubes running under pulsed conditions.

The last stage in the fabrication of a cathode is the deposition of the cathode paste on to the cathode base. The methods of spraying, cataphoretic coating and painting are well known, but if the correct particle size has to be maintained on the cathode surface, meticulous care must be exercised in these processes. In particular, the study of the aerodynamics of spray guns has led to a design of guns spraying uniform coatings under mass production conditions with a reproducibility hitherto unattainable.

Other methods of placing the cathode coatings on the cathode base, still in the development stage, promise increased density of coating coupled with a smoother surface. Some of the new cathodes show emission characteristics more nearly approaching those of the hollow type of cathode than the ordinary oxide cathode.

Testing by Mass Spectrometer

The mass spectrometer is being used in the valve industry to a rapidly increasing extent. Its uses fall into the main categories—of obtaining a qualitative analysis of the gases evolved in a valve during processing, and leak testing.

The mass spectrometer gives information on the time of baking necessary to reduce the evolution of harmful gases from the assembly to an acceptable minimum. It can also be used to estimate the time taken to eliminate these gases after processing the cathode. Generally, the mass spectrometer lends itself to the investigation of troubles which inevitably occur in valve manufacture. Apart from mechanical failures, the main causes of trouble are chemical, and the instrument can detect the source of residual gases which may be present in the valve.

Leak testing with the help of the mass spectrometer is applied particularly in the case of the more expensive valves such as magnetrons, klystrons, or special tubes, where a failure in manufacture is serious. Leaks of the order of 3×10^{-10} l./sec. may be found by probing with helium for only 10 seconds. The speed with which small leaks may be detected compares very favourably with other leak testing devices which have been reported.

For quantitative measurements on gases evolved from a valve some form of collection of the gas is required, and this is done with an auxiliary diffusion pump which will concentrate the gases in a vessel which can thereafter be opened to the instrument.

To examine the gases in a valve which has been sealed off from the pump, the envelope has to be broken under vacuum. This can be achieved by allowing a weighted iron slug with a sharp point to be rammed against the tube by energising an electromagnet external to the vacuum system.

Much work is still required to make the mass spectromer a really versatile instrument for the valve industry. Efforts should be concentrated (1) on making the volume of the system small so that it is comparable with the volume of the valve to be examined, (2) on reducing the background pressure below the pressures usually found in gettered valves, and (3) on reducing the contaminations due to greases from taps and from glass. Some form of omegatron or other radio frequency mass spectrometer may find increasing application in the valve industry. The usual contaminants traced by mass spectrographic analysis in glass are water vapour, carbon monoxide and small quantities of carbon dioxide. As the temperature of the glass is increased from room temperature to near the softening point, the output of these gases increases, but higher mass

numbers appear which are attributed to products of the decomposition of the glass, and of the hydrocarbons of the oil employed in both the diffusion pump and the backing pump[17]. These contaminants have been found to be present whenever the glass is allowed to get hot so that any analysis of gas from metals done in glass envelopes, must take into account the possible background originating from the glass. The evolution of water vapour from glass appears to continue over very long periods.

The predominant gases evolved from nickel are carbon monoxide and hydrogen, but there is also some water vapour, and smaller quantities of oxygen and carbon dioxide.

The evolution of gas on heating is very rapid and about one-third to a half of the total amount is given off in the first few minutes of heating at 400°C.

Almost equally fast is the rate at which gas is taken up by a thoroughly degassed sample of nickel when it is stored either in a moist or dry atmosphere. Within one hour, the metal may have again absorbed its maximum quantity of gas. The proportion of carbon dioxide to carbon monoxide, however, may be greatly increased.

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RECENT RESEARCH DEVELOPMENTS

Pumping by Ionisation Gauges

Research in the valve industry has been stimulated in recent years by the development of a technique of pumping to pressures as low as 10^{-10} mm. Hg, at which pressure the number of molecules is reduced to 3.3×10^{6} per c.c. and the probable interval between collisions of two molecules is increased to half an hour.

The ionisation gauge pumping technique has been briefly described in a previous section. The mechanism[18] has been investigated both practically and theoretically. The curve showing the reduction of pressure with time, as an ion gauge electron current is started by switching on the voltage to the grid, is given in Fig. 7. In the same graph the recovery of pressure is shown, as the electron current is switched off after pumping for a short time. It is seen that on switching on the current there is an immediate fall in pressure which, in some gauges, has been of an order of 10 below the initial pressure, followed by a slower fall in pressure which continues as long as the current is run. Similarly, when the current is switched off after running for a very short time, the pressure quickly recovers to its original value. If the current is not switched off until many hours or days have elapsed, then the recovery of pressure is very slow and incomplete.

The mechanism proposed for the pumping action is that in an enclosed volume, a fraction αi of the total number of molecules are removed by pumping to the interior surfaces. Of these, a fraction γ/α are re-introduced into the free space after sticking to the surface for a time given by $1/\beta$. In addition, the glass walls and other surfaces are assumed to desorb molecules as the pressure is lowered during pumping, in an effort to restore the former pressure. The rate of desorption is assumed to be proportional to the difference between the initial and instantaneous number of molecules in the system, the constant or proportional factor being denoted by δ. When the current is switched off and the pressure recovers, β and δ become β^* and δ^*.

With these assumptions, it can be shown that the pressure changes on short-term pumping and recovery from pumping may be represented by the sum of two exponential expressions as follows

$$p-p_1=C_1e^{-a_1t}+C_2e^{-a_2t} \quad \text{for pumping}$$
$$\text{and} \quad p^*_0-p=C_1^*e^{-\beta^*t}+C_2^*e^{-\delta^*t} \quad \text{for recovery}$$

where p_1 is the final pressure after pumping, and p^*_0 is the initial pressure after recovery starts, a_1 and a_2 are the roots of the equation.

$$x^2-(\alpha i+\beta+\delta)x+\beta\ ((\alpha-\gamma)\ i+\delta)=0$$

$C_1C_2C_1^*$ and C_2^* are constants depending upon α,β, β^*, δ and δ^*, and i is the pumping current.

A typical curve is given in Fig. 8 of the factor p^*-p_0 during recovery of pressure after an ion gauge electron current has been switched off. The coefficients β^* and δ^* may be obtained since after

Research into Manufacturing Problems I. Ion Gauge Pumping

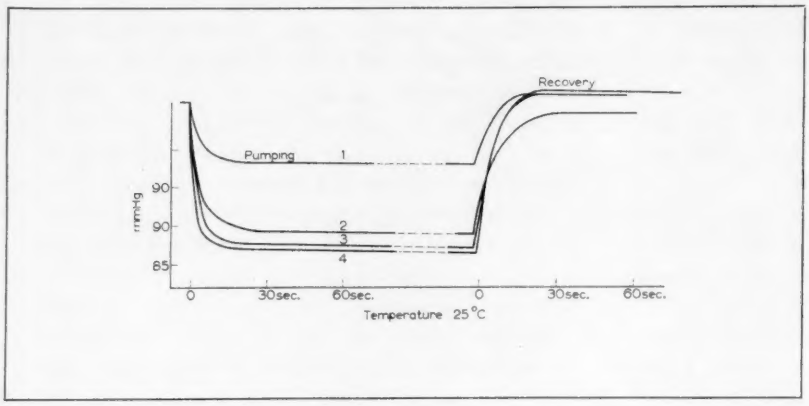

Fig. 7. Indicating recovery after a short period of Pumping. Electron currents: 1—3 mA, 2—5 mA, 3—7 mA and 4—9 mA

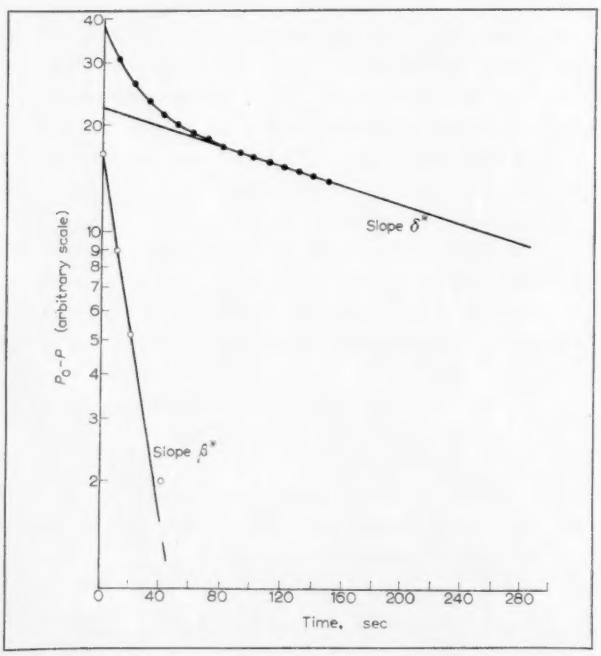

Fig. 8. Variation of pressure with time on recovery after short-period pumping. Factors δ^* and β^* are derived from these curves.

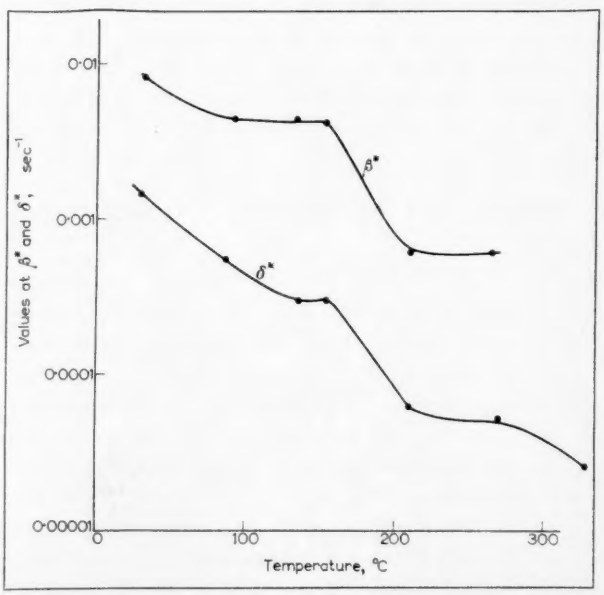

Fig. 9. Variation of δ^* and β^* with temperature. δ^* is a factor depending largely on the properties of the glass envelope and $1/\beta^*$ is the sticking time of residual gas molecules on glass.

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30—40 seconds the curve is a straight line with slope δ^*. By difference the slope β^* of the first exponential term may be obtained. Values of β and δ may also be obtained indirectly from similar curves, but the method involves two graphical solutions and the accuracy is not so great. Fig. 9 shows the variation of β^* and δ^* with temperature of the system. It is seen that there is a rapid fall in β^* and δ^* as the temperature rises to 100°C from ambient. There is a stationary region in the neighbourhood of 100—150°C and then a further fall at high temperature. Measurements show that the proportion of ions trapped by the glass is usually greater than that captured by the collector. The factors β_1, β^*_1, δ, δ^*, are largely properties of the adsorption of the residual gases and glass. The factors β and δ vary in a similar manner to β^* and δ^*.

The heat of adsorption of the residual gases on glass may be calculated knowing the sticking time $1/\beta^*$ from the Frenkel equation.

$$1/\beta^* = \tau_0 \text{ Exp. } (Q/RT)$$

where τ_0 is the usually accepted figure of 10^{-13} sec., Q is the heat of adsorption, R is the gas constant and T a given temperature.

Values of Q ranging from 20 to 40 Kcal/mol (0.87—1.74 eV) are obtained as the temperature rises from 30—300°C. These values fall well within the range of accepted values for atmospheric gases on glass.

This method can be generally applied to all types of tube, and analysis of pumping and recovery curves may lead to the detection of abnormalities in residual gases and in surface conditions.

Long pumping by ion gauges will gradually reduce the pressure in a closed system to a value limited only by the diffusion of helium from the atmosphere and by the gradual desorption of gases from parts of the assembly. Pressures of 10^{-10} mm. Hg or less can be obtained as a result of routine procedure.

Gas Adsorption and Desorption

Low pressure in the 10^{-10} mm. Hg region, and the means of measuring such pressures, make it possible to trace the behaviour of adsorbed gases in a closed system. There are a few substances which can be cleaned sufficiently well to remove all the adsorbed gas molecules from the surface. Of these, tungsten can be taken as a typical example, since it can be heated to 2,500°C at which temperature the surface molecules are desorbed, and yet there is little evaporation of tungsten from the surface. The clean tungsten surface becomes contaminated at a rate determined by the bombardment by residual gas molecules which, at a pressure of 10^{-10} mm. Hg, would result in a complete monolayer of gas being formed in seven hours, if it is assumed that every molecule which hits the tungsten sticks to it. For a quarter of this time therefore the surface could be considered clean. At a pressure of 10^{-11} mm. Hg the surface would be fully contaminated after 72 hours. Thus application of high vacuum techniques now makes it possible to determine adsorption coefficients of gases[19] on surfaces, contact potentials, secondary emission coefficients, etc., by measurements obtained from surfaces which can be trusted to be clean. The low pressures may be attained by high temperature baking and ion gauge pumping without the use of orthodox getters, but glass itself proves to be an extremely good getter at low pressures for some gases normally adsorbed on metals. Indeed, glass may take a very active part in gas exchanges at this pressure level.

If a tungsten wire is heated at a pressure of 10^{-10} mm. Hg to a temperature of about 1,200°C, the resulting pressure changes in the glass envelope, as illustrated in Fig. 10.

A small peak is observed at A, a much larger peak at C, and the pressure finally levels off at D. Repeating the measurements the peak heights at A and C may be different, depending on the length of the cold interval following the last heating up of the wire. If the cold interval is very short, then the peaks at A and C may be absent and only the level D is reached. The magnitudes of A and C depend upon the cold interval, but that of D is independent. If the wire is heated to a maximum temperature of only 800°C, then the peak at A is found to consist of

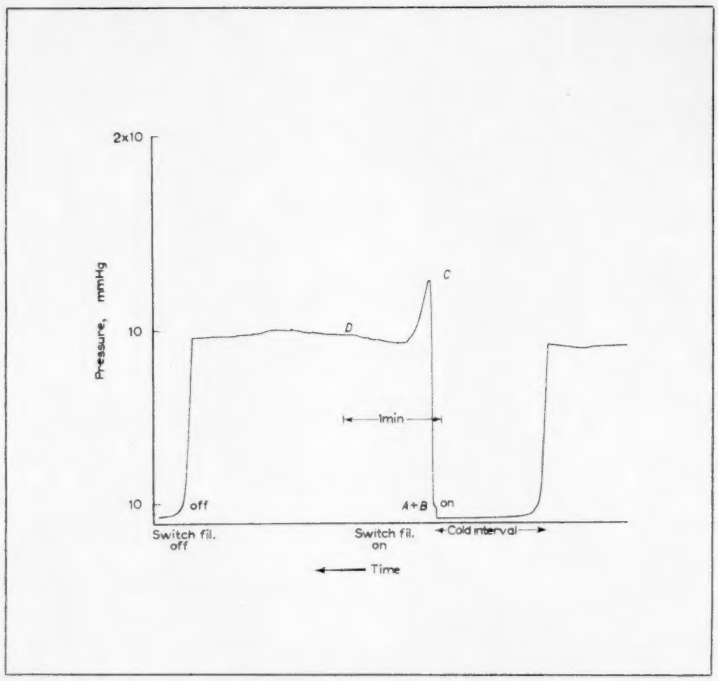

Fig. 10. Record of pressure changes in an enclosed volume when a tungsten filament is flashed at 1,156°C. in a background pressure $< 10^{-10}$ mm. Hg. The final part of the trace shows the behaviour on switching the filament off.

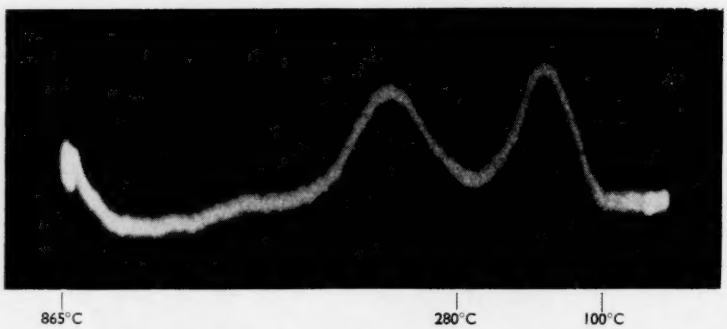

Fig. 11. Record of the pressure changes in an enclosed volume when a tungsten wire is heated. The two peaks appear in Fig. 10 as a single peak A. The rate of adsorption by the glass is the same for both desorbed gases.

two separate peaks A and B, and peak C is completely absent.

The resolution of the desorption peaks A and B may be improved by a method described by Hagstrum[6]. The filament under investigation is connected to one arm of a wheatstone Bridge. The out-of-balance current is detected by the X plate of a C.R.O. An ion gauge measures the pressure in the system and its output is recorded on the Y plates. The bridge is first balanced at a low voltage so as not to heat the filament, and then a higher voltage is suddenly applied. The resulting C.R.O. trace gives a record of the pressure in the system as a function of the temperature of the filament. Fig. 11 shows peaks A and B measured by this method.

Combining all these results, it is seen that there is evidence of at least four gaseous phases resulting from heating a tungsten filament to 1,200°C. All but one gas, that of phase D, are very quickly adsorbed by the glass and, in the case of phases A and B, the rate at which adsorption takes place is the same. The whole phenomenon of adsorption takes place in a small fraction of a second. The gas phase C gives the most prominent peaks, but again the gas is re-adsorbed in a matter of seconds. The phase D is not adsorbed by the glass, but is readily re-adsorbed by the tungsten filament when it cools down. It is calculated that the time taken to re-adsorb all the molecules giving rise to the pressure shown at D, is 10^{-4} sec which is too short for the recorder to measure. The phases A and B may be the same gas, since their rates of adsorption are the same, but the temperatures at which they are desorbed points to different heats of adsorption which may arise from two kinds of adsorption sites on the tungsten surface. Phases C and D may be different residual gases.

The transient gases desorbed from a tungsten wire are important because they appear at low temperatures and may occur whenever a valve with a tungsten heater is energised. These gases may poison the cathode since there is some evidence that one of them may be carbon monoxide.

Transient gases have also been detected from nickel and molybdenum.

Sputtered Films on Glass

The evolution of gases from glass in tubes is reduced by covering the surface with sputtered metal films of molybdenum or aluminium. Mass spectrographic analyses[20] have been made of the gas output from glass sputtered with metal films and compared with the gas output from plain glass. Identical bulbs were heated and the gas evolved from each recorded on a mass spectrometer. One of the bulbs was sputtered with a metallic film by passing a discharge in neon gas, and then evacuated. Both bulbs were again heated and it was found that the gas evolved from the bulb with sputtered molybdenum films is reduced to less than 1% of that from the unsputtered bulb. The effectiveness of the films of different metals vary with temperature but they can be placed roughly in the following order:

> Magnesium, molybdenum, aluminium, zirconium, tantalum, nickel, fernico, *glass*, gold copper.

The first three metals are extremely effective and may reduce the water vapour evolution by a factor of 100 or more at elevated temperatures. Gold and copper appear to increase the evolution of water vapour.

The process whereby gas evolution is reduced for most metals is not known but it may be a combination of two mechanisms. The sputtered film may either prevent gas diffusing out of the glass or adsorb it as rapidly as it diffuses out.

The properties of molybdenum films[21] have been known for some time and have been used successfully in stabiliser valves where a discharge is maintained between molybdenum electrodes in a glass bulb heavily sputtered with a molybdenum film.

Any contaminating gas which would normally be adsorbed by the electrode will now be adsorbed very largely by the molybdenum film; in addition there is the sealing action of the film, hence the electrode surfaces remain unchanged during life and consequently the burning voltage is very stable. Molybdenum sputtered films have also been used in experimental work as getters, and have enabled very low pressures to be attained.

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The metal films must not be allowed to oxidise, otherwise their effectiveness is almost entirely lost. This limits the application of the technique to valves in which the metals can be sputtered *in situ*.

CONCLUSIONS

The subject of vacuum in industry is a vast one and the foregoing has dealt with only a few selected aspects. The main principles of attaining and maintaining vacua are likely to remain unchanged for a considerable time. Stringent control of materials and meticulous care in assembling and pumping are the essential secrets leading to successful valve manufacture.

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THE GETTERING PROCESS
in modern receiving valve manufacture

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Summary

GETTERING TECHNIQUE and getter performance as far as it comes within the sphere of the valve processing engineer is discussed. A brief review of getter design development is given. This is followed by a critical discussion of the 'ideal' requirements of the valve manufacturer compared with the actual processing properties of the various modern getters such as the stirrup getter, the coated and the sintered ring getter. Brief reference is made to the testing of getters and to the absorption characteristics of ring getter deposits.

Sommaire

LA TECHNIQUE ET LE RENDEMENT DES GETTERS dans le domaine de la fabrication des valves sont discutés. Un bref rappel est fait sur leur développement, suivi d'une discussion critique sur les éxigences des fabricants de tubes électroniques concernant le getter 'ideal', comparant les propriétés des différent modèles de getter telsque le getter d'étrier, le getter fritté en forme d'anneau, etc. Brèves réferences sont données sur l'essai des getters et les caractéristiques d'absorption des dépôts provenant des getters en forme d'anneau.

INTRODUCTION

THE GETTERING PROCESS may take only an insignificant fraction of the total time and labour spent on the completion of an electronic valve but nevertheless high quality gettering is an imperative requirement to guarantee initial and sustained operation of the valve in accordance with its stipulated electrical characteristics. The gettering properties of certain metals have been discovered as early as seventy years ago but the methodic utilisation of such properties as part of organised industrial production procedure is only about thirty-five years old and has grown in step with the expansion of thermionic valve manufacture.

Going back over the history of gettering technique, surveyed in detail in the following section, it is interesting to note the remarkable position the metal barium has assumed in the course of development as the most popular gettering material. Today, with the exception of a few instances where getter deposits within the valve and, consequently, getter evaporation are inadmissible, barium is virtually without a rival in the whole of the valve manufacturing industry. Like other workers before him the author has investigated many alternative metals such as those indicated by Espe, Knoll and Wilder[1], studying their performance either in the solid state or after evaporation and deposition. Some of these metals may show reasonable adsorption capacities when raised to a temperature of 1,000°C or thereabout, but the gettering power of barium at its best is never reached. Barium, unlike any other metal investigated in the course of time, is a getter material effective universally, *i.e.* it will getter any gas more or less efficiently. In addition, some research workers claim—and we agree—that it

*MS. received April, 1958.

getters irreversibly when operated at temperatures not exceeding 400°C. Finally, an important consideration from the industrialist's point of view, most modern barium getters are reliable, economical, uniform in their performance characteristics and of extreme versatility in their use, *i.e.* capable of meeting operational conditions in an infinite variety of valve types.

Present-day knowledge on the physical and chemical phenomena governing performance characteristics of barium deposits have been discussed in previous contributions to this journal.[2–4] Here, we shall examine the different types and designs of getters available today and enter into a critical discussion of their actual 'processing' characteristics in the light of what is termed, for the purposes of this study, the 'ideal' requirements of the valve processing engineer. At the same time we will examine the circumstantial processing conditions, under which the getter is fired and deposited, and means of controlling getter processing characteristics effectively.

The information given in this paper applies exclusively to valves with glass envelopes. It does not embrace gettering techniques or conditions encountered in cathode-ray tube manufacture and essentially applies to the conditions prevailing in receiving valve manufacture of the miniature type.

GETTER UNIT DEVELOPMENT

The first to employ regularly the gettering properties of materials in industrial production was Malignani[5] who, in 1894, initiated the use of a suspension of red phosphorus for the improvement of the vacuum in incandescent lamps. This method is still in use today in that industry but, because of the high vapour pressure of the phosphorus, is not applicable in the case of thermionic valves.

The earliest scientific appreciation of gettering phenomena, known to the author, dates back to 1883 when Fitzgerald in the U.S.A. was granted a patent protecting his discovery of the gettering action of magnesium. Soon after, certain metals, especially those of the rare earth group, were found to have gettering properties and in 1905/1906 Soddy was granted two U.S. patents, No.17933AD dealing with gas absorption by the evaporation of calcium and No.5349AD dealing with the gettering properties of barium. The results of the work leading to these patent applications paved the way for the introduction of the gettering process in thermionic valve manufacture as we know it today.

The original industrial getter consisted simply of a length of magnesium wire which was mounted directly on the anode and was evaporated 'naturally' during the degassing treatment of the latter. The hot magnesium vapours being active, an improvement in the vacuum was obtained but the results were not spectacular. The cause for this inadequacy was traced back to the fact that during degassing the anode gives off gas, of a nature and in quantities, such that the absorption properties of the rising magnesium vapours are limited as they are partly saturated and partly inhibited before the intended gettering action can take place. The realisation of these conditions resulted in the development of a proper getter unit consisting of the actual getter held in a supporting structure of its own[6] and thus facilitating the mounting of the getter unit anywhere in the valve, away from the anode. The first getter unit of this kind was marketed in 1927. It was quickly followed by further improvements based on the realisation that barium was of a higher activity than magnesium and, in 1929, Kemet introduced a getter unit containing barium alloyed to magnesium. Due to the success of the latter, getters of various barium-alloy compositions were put on the market in the period immediately following and, as the introduction of these getters coincided with a rapid expansion of the valve industry, their development contributed substantially to the establishment of getter manufacture as an industry in its own right.

The barium-magnesium getters of that period consisted of *tablets mounted on a nickel flag* which was joined to the electrode assembly of the valve, see Fig. 1 (a) and (b). When fired the magnesium evaporated at the comparatively low temperature of 600°C and the magnesium vapours carried a

certain amount of free barium with them. However, prolonged experience with this type of getter established two important drawbacks: The quantity of free barium becoming available for gettering action was comparatively small within the permissible temperature range. High temperatures or impurities present in any quantities on the inner surface of the glass envelope, would cause the magnesium deposit to peel off and result in magnesium flakes migrating across the interior of the valve, thus rendering the valve unserviceable.

The recognition of these drawbacks gave birth to the development of the so-called *pellet getters*, the first of which became available in the same year.

In its original form this getter consisted of pure barium melted down in a thin-walled copper tube which was subsequently drawn to an outer diameter not exceeding 1-4 mm. The tube was sealed at both ends and stored under vacuum or submerged in paraffin wax. Immediately prior to use the tube was cut up into pellets not exceeding 5 mm. length and the pellets were welded to nickel flags for assembly in the valve. While this getter met the requirements of the day by making an appreciably larger quantity of barium available for gettering in the tube and at the same time disposing of the disadvantages caused by the presence of magnesium, its effectiveness was considerably less than expected. It was found that a substantial portion of the barium was spoiled prior to use due to lack of stability after cutting of the pellets, poisoning effects during the heat treatment of the valves after assembly and, also, some degree of alloying of the barium to the copper in the initial manufacturing stage of the getter unit.

Later modifications of the pellet getter provided for the substitution of copper by nickel and iron as tube material, in an effort to overcome some of the disadvantages mentioned but all versions had one major fault in common, *i.e.* the pellets lacked stability in air. Also, these getters are expensive because of the need of flag mounting. However, the fact remains that this type of getter has been widely used for many years. Indeed, in all cases where it is imperative to dispose of a large quantity of barium in order to getter a valve efficiently, its

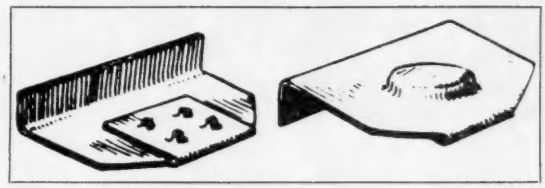

Fig. 1(*a*). Two versions of mounting tablet getters on a heater.

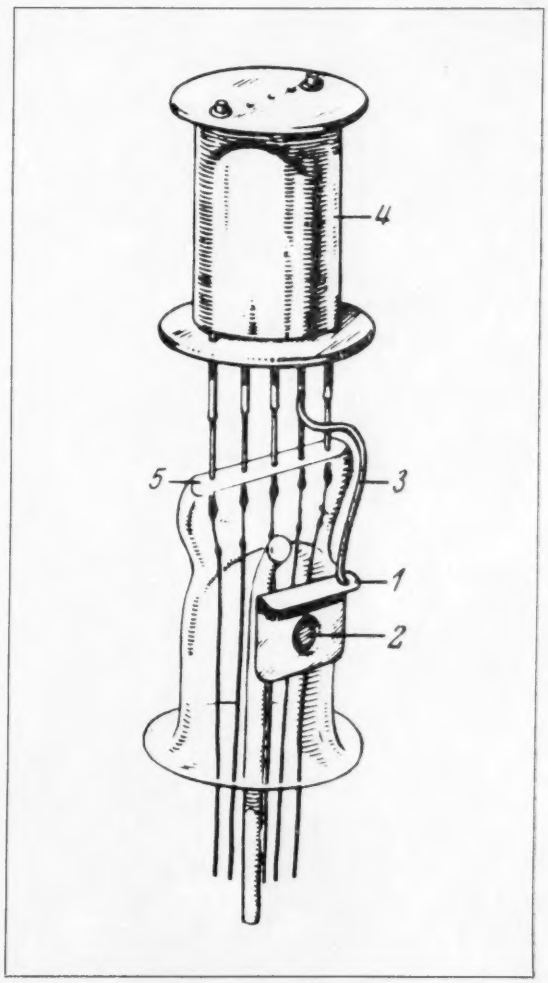

Fig. 1(*b*). Getter assembly in operational position. 1—heater; 2—tablet getter.

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popularity was virtually unimpaired by any novel developments in getter design until very recently.

All pellet getters discussed so far consist of a charge of pure barium in a suitable metal envelope. The remaining two to be mentioned follow the modern conception of providing a suitable barium-alloy charge.

Telefunken in Germany developed during World War II the so-called barium-thorium getter, the pellets consisting of a barium-aluminium-thorium alloy. Its absorption capacity appeared to be outstanding but stability in air was lacking and, as a result, handling was dangerous. Production of this getter has been discontinued.

Barex developed a tablet getter recently which is

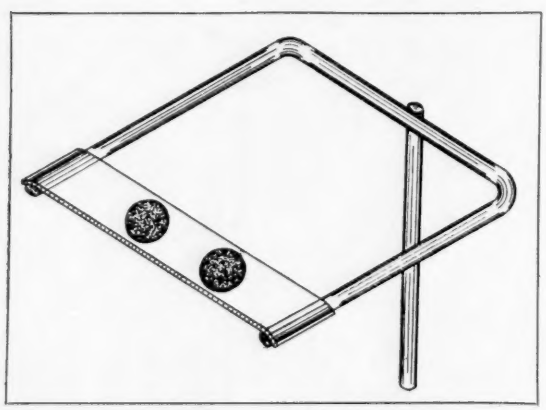

Fig. 2. Barex Pellet Getter.

remarkable for the high quality of its barium-alloy charge and the wide range of types in which it is made available, see Fig. 2. Three of the most popular Barex getters have the following composition; 'F'—25% barium, 20% aluminium and 55% magnesium; 'D'—37% barium, 43% aluminium and 20% magnesium; 'A828'—40.3% barium, 36.3% aluminium, 3.4% calcium, 11% iron and 9% nickel.

Before leaving the subject of pellet getters reference should be made to tablet getters of the non-barium type such as those consisting of alloys of titanium and zirconium. A modern version is the 'Ceralloy 400' getter consisting of cerium and thorium painted on and sintered. Information on this getter can be obtained from a lecture delivered recently by Briggs*. These getters are of the non-evaporative type and their use is essentially restricted to the aforementioned few applications where a deposit of a metallic mirror on the valve envelope should be avoided. They have an appreciable absorption capacity but at the same time the distinct disadvantage of operating selectively, *i.e.* absorbing only a limited number of gases.

Another group of getters, frequently discussed in the literature and representing a great advance in the art at the time of their introduction, are the so-called *reactive getters*. Lederer[7] was the first to suggest such a getter which consisted of a mixture of barium strontium carbonate sprayed onto a strip of tantalum by a method essentially the same as that applied in the preparation of oxide cathodes. The tantalum reacting with the carbonate liberates carbon dioxide and pure barium. An inherent disadvantage of this method is the considerable gas evolution occurring during the reaction and in order to reduce the amount of gas evolved Wamsley[8] proposed the barium berylliate getter. Fig. 3 shows a Batalum getter (manufactured by R.C.A.) which represents the most advanced type of this family of getters.

Although the amount of barium becoming available for gettering in the valve is satisfactory, the considerable gas emission occurring in the course of the reaction constitutes an inconvenience great enough to allow for the use of this type of getter on a limited scale only. However, this getter is regularly applied in tubes where the firing of the getter has to be effected by a current of low magnitude *via* a separate electrical circuit.

By and large, one is justified to say that mention of the reactive getters closes the account of such getters which from today's point of view seem to have essentially an historical interest. There are few applications where the getters already discussed have not been superseded by new designs developed during recent years. Almost the whole

*T. H. Briggs of Briggs Associated, Inc., Norristown, Pa., U.S.A. The title of the paper is 'Continuous Getters for Electron Tubes' (Sept. 1956).

range of industrial gettering tasks today is served by one or more of the following three types, the stirrup getter, the coated-ring getter and the latest newcomer, the sintered-ring getter.

The Kic getter put on the market by Kemet in 1938 (Brit. Pat. No. 492,529) is the first of a series of *stirrup* getters which for the reason of its versatility in practical use met with considerable success, see Fig. 4. Its conception constitutes a direct development of the iron tube pellet getter. In its early design the charge was pure barium but in a later form it is a barium-aluminium alloy and the tube containing the charge is drawn to a diameter smaller than that of pellet getters. In addition, one portion of the tube circumference is ground flat so that the barium vapours may escape through the gap in the metal container, which is formed when, on firing the ground portion of the container wall melts away. It appears, however, that at least in the early stages of the production of this getter unit, the flashing mechanism did not operate in all cases as intended[6]. Frequently the gap did not form and the barium vapours issued instead from the open ends of the getter bar.

An attempt was made by Philips to overcome this difficulty when developing the stirrup getter marketed under the name of Phic[9] getter during the year of 1948 (see French Pat. 974,302). As can be seen in Fig. 5, grinding down of the tube wall has been abandoned in favour of machining a groove into the wall extending over the whole length of the container. In practice, machining of the groove accurately enough to ensure without fail the formation of a gap on firing proved extremely difficult and no substantial progress seems to have been made in this respect as the manufacture of this getter has been discontinued.

Third in the series of representative stirrup getters is the St2 unit developed by the company of the author. Fig. 6 gives a detailed drawing of the getter. The idea of a fully enclosed tube-shaped getter container is replaced by a permanently open trough container, thereby disposing of all manufacturing difficulties inherent in the two previously described designs. Reliance on proper preservation

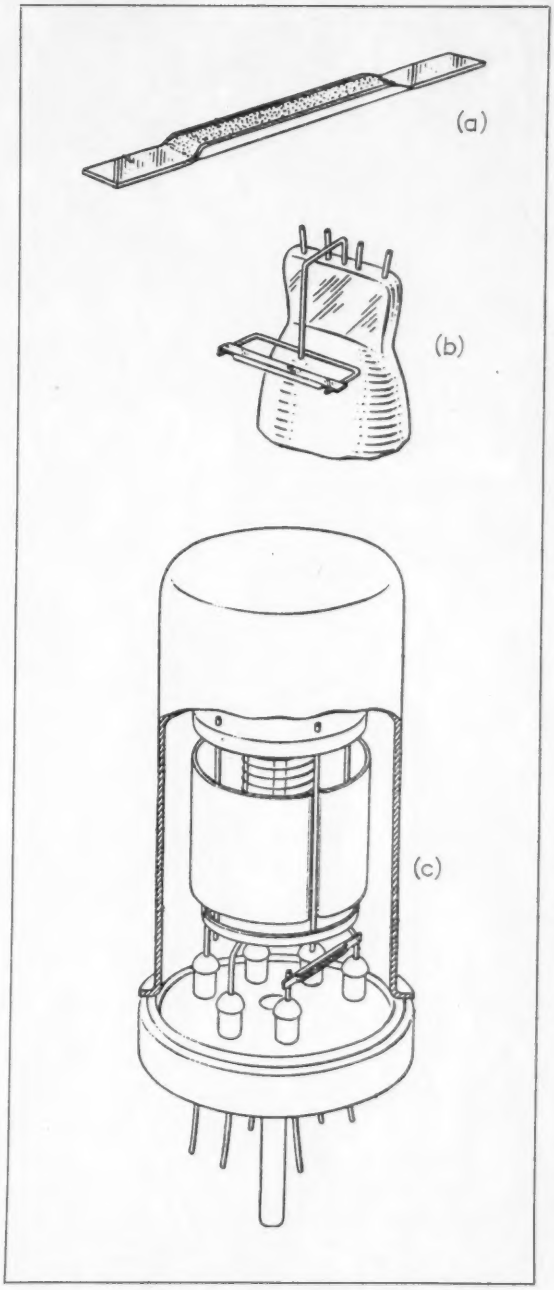

Fig. 3. Strip Batalum getter (*a*) mounted on the valve support, (*b*), the mounting for direct heating is shown in (*c*). (From the Patent Specifications).

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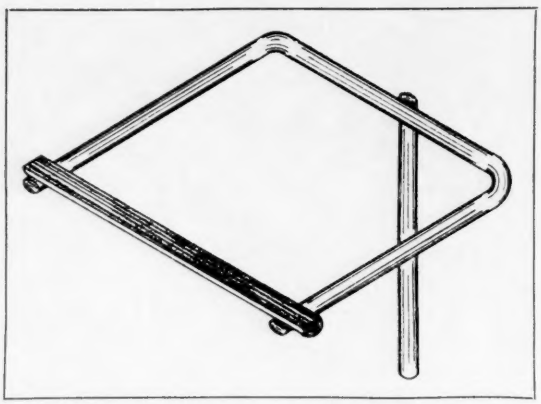


Fig. 4. 'Kic' Getter—Simes 'Gov'.

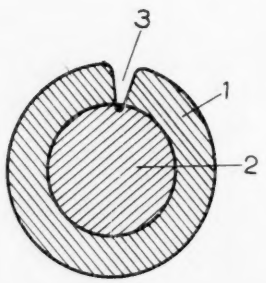
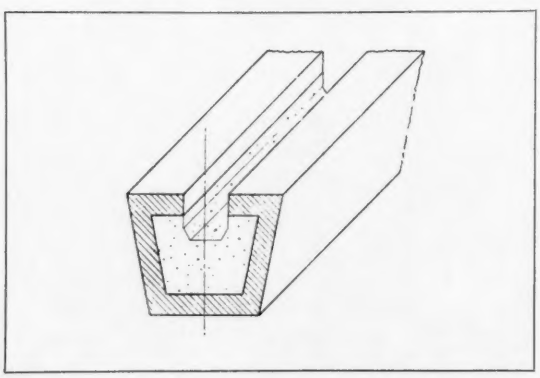


Fig. 5. Section of the Philips Getter (Phic). 1—Iron tube; 2—core of active alloy and 3—groove.

Fig. 6. Section of the St2/F/v—type of SAES Getter magnified ×20.



of the getter material is placed entirely on the stabilising properties of the alloy used as the charge. The barium content of the troughs varies from 2-6 mg. per cm. length of trough. The St2 design has the additional advantage of providing some directional control of the barium vapours during flashing.

The logical sequence to the development of stirrup getters incorporating a straight getter container bar is the evolution of the *ring getter*, of which there are two different versions available on the market today.

The first, illustrated in Fig. 7, is manufactured by Telefunken and consists essentially of a nickel-plated iron ring carrying a coating of an alloy of 50% barium-aluminium and 50% iron-thorium, collodion being used as the bonding agent to secure proper adhesion. The second, an S.A.E.S.[10] product (Brit. Pat. No. 736,475), is of similar appearance as can be seen from Fig. 8. The charge is a barium-aluminium-nickel alloy and the only other essential difference between the two ring getters refers to the method of applying the coating representing the charge to the ring. As will be discussed in greater detail in a subsequent section the use of a bonding agent is inconvenient as its presence causes extra gas emission when the getter is fired. The present design therefore provides for the application of the getter charge to the ring by a sintering process.

It can be assumed that stirrup getters and ring getters employing a barium alloy charge can cope between them with all gettering propositions presenting themselves in industry today. The remainder of this article, therefore, is restricted to a consideration of the merits of stirrup and ring getters with respect to the various problems and tasks discussed in the subsequent sections.

However, before concluding this survey the author would like to give due emphasis to one particular phase in the developments just described.

The above survey has indicated the great number of difficulties encountered in getter development and the type of solutions applied to overcome them. The main goal is, of course, to ensure that, appropriate to the task, barium with unimpaired activity

and in sufficient quantity is liberated from the unit when firing the getter. The most decisive step towards securing this objective is the introduction of barium alloys as getter material and, in particular, the introduction of barium-aluminium alloys. The first factual mention of barium-aluminium alloys as getter material seems to have been made in U.S. Pat. No. 2,018, 143. The advent of alloyed barium materials disposed effectively of the ever-present problem of the stability of the getter material in air. It facilitated manufacturing getters without the risk of deterioration during production, and safe handling of the same during processing by the consumer. Strangely enough, as far as the author knows, no proper tribute has ever been paid in the literature to the implications of this important step in getter development.

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THE GETTERING PROCESS

Modern receiving valve manufacture is a mass production proposition. There are factories which make up to 200,000 valves a day. It is estimated that nearly 95% of all receiving valves produced are of miniature size and there is a large variety of types distinguished by their electrical characteristics. Fortunately, there are few differentiations with regard to the geometrical characteristics of the various valves and thus, a potentially large variety of final processing techniques is reduced in practice to a few methods uniformly applicable to a large number of valve types, comprising one group in each case.

The Operational Conditions

Exhaustion of the Valves. Assembly, exhaustion and sealing-off of the valve is normally carried out on the so-called Sealex indexing-type of machine, where the work holder carrying the valve moves on a circle conveying it from one operational station to another until the valve is completed. The machine is fitted with all the provisions necessary to carry out all subsidiary processes required in the final stages of valve production, such as gas burners and high frequency coils.

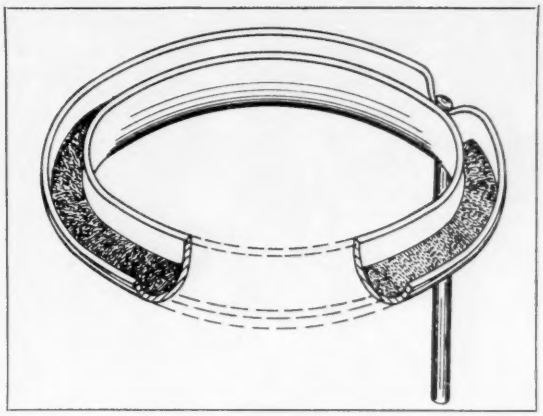


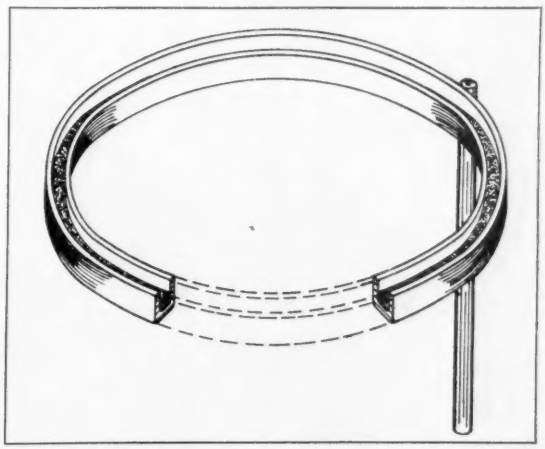
Fig. 7. Telefunken Ring Getter.

The pumping systems employed vary and are given below in the order in which they were introduced in industry:

(*1*) Pumping means: Mercury diffusion pumps. Arrangement: One diffusion pump for each pumping station. The diffusion pumps are connected either to a central fore vacuum supply installed in the building or to rotary pumps especially fitted to the particular machine.

(*2*) Pumping means: Two-stage rotary pumps. Arrangement: Every pump serves one or

Fig. 8. SAES Ring Getter.



more pumping stations or, alternatively, a single pump is connected to a manifold which in turn is in communication with the valves being processed.*

(*3*) Pumping means: Oil diffusion pumps.
Arrangement: As distinct from (*1*) and (*2*), each valve is connected to a complete pumping unit, *i.e.* a unit including the mechanical fore vacuum pump. This method follows the technique used in the evacuation of kinescopes.

The primary purpose of the evacuation process, of course, it to remove the atmospheric air present in the valve envelope originally, but, in addition, it serves to remove the gases which evolve in the course of processing the valve.

Gas evolution is initiated and progressively increased as the pressure in the valve is being reduced. Towards the end of the pumping process, it is artificially accelerated to a maximum rate by means of a special degassing treatment where the glass envelope is exposed to gas flames and the metal components of the valve are heated by high frequency induction currents. It follows the process of activating the oxide-coated cathode which, in turn, accounts for the fresh evolution of considerable quantities of gas, essentially carbon dioxide this time. Finally, immediately prior to sealing off the valve, in some cases the getter is outgassed at a dull red heat equivalent to about 600°C. The gas evolution at this stage varies appreciably in accordance with the type of getter used. It depends, first of all, on the quality of stabilisation achieved in the particular getter alloy but further on the methods employed in getter production and, in particular, on the rigour of the degassing procedure applied prior to the delivery of the getter. As a rough guide, modern getters can be expected to have a gas emission of approximately 1μl./mg. barium content and there are many instances today, where the outgassing of getters *in situ* can be omitted altogether.

In modern industrial establishments it is the prevailing practice to seal off the valve prior to firing the getter. The advantages offered by this procedure, *i.e.* by operating the getter after the valve has been closed, was discussed in a previous contribution[2]. Sealing of the valve is effected when the pumps have obtained a pressure of 1×10^{-3} mm.Hg which is a convenient pressure value as will be explained in the following section.

Task of the Getter. It is thus the task[1] of the getter to reduce the pressure in the sealed-off valve from the aforementioned value to that required operationally, *i.e.* to a value not higher than 1×10^{-7} mm. Hg.

In this connection we should consider the impedances introduced in the pumping line by the limited capillary conductance values of the pumping stems normally employed in valve production. The stems are joined to the tube while processed on the indexing machine and are sealed to the bottom of the valve in the case of G*-types and GT*-types, and sealed to the top of the valve in the case of the miniature and subminiature sizes. Table I gives the dimensions of pumping stems employed in practice and shows that the conductance values occasioned by the tolerances allowed in the diameters of the stems, vary considerably, sometimes by a factor of 4. As is known, the value of the capillary conductance of the stem determines the speed at which the valve can be evacuated, irrespective of the capacity of the pump employed in the process. On the other hand, the rate at which the getter is 'pumping', exceeds that given by the stem conductance in the pressure region of 10^{-3} to 10^{-4} mm. Hg. This, therefore, is the pressure region, where it is convenient in practice to seal off the valve and to let the getter take over from the pumps.

After sealing-off, the valve is allowed to cool down to room temperature. During this period the vacuum in the valve improves appreciably. This is due to two causes. Firstly, the kinetic energy of the residual gas atmosphere is reduced, in step with the fall of the temperature. Assuming a temperature of 200°C at the sealing-off stage, the pressure in the valve will be reduced by 38% on this account alone,

*For final pumping, more up-to-date arrangements of this type provide for the use of diffusion pumps.

*The GT-type of valve is strictly cylindrical and the G-type has an envelope, the diameter of which is not consistent.

when room temperature has been reached. The total reduction of the pressure, however, will be substantially higher due to the re-absorption of gas by the valve surfaces, which is particularly strong after completion of the degassing treatment.

In the case of flashing after sealing-off, the getter is fired at room temperature. Inevitably during this process a fresh quantity of gas is evolved but, since stabilised getter alloys have been introduced, the amounts liberated are small enough not to interfere with the proper action of the getter unless the getter is faulty.

In the past it was a common belief that the action of the getter is essentially confined to the vapour state, *i.e.* to the flashing phase of the getter. However, recent investigations have confirmed that gas absorption during that stage is negligible, unless the vacuum in which the getter is fired is particularly poor. The latter is indicated by the mirror deposit acquiring a blackish appearance as a result of porosity.

Under normal processing conditions it can be expected that the pressure in the valve is reduced to 1×10^{-6} mm.Hg. in the period immediately following the flashing of the barium vapours. This is followed by a steady improvement progressing at a slower rate and yielding a pressure of 1×10^{-9} mm.Hg in the course of a few days.

Remarks on Getter Deposit Siting. In receiving valve production some difficulty is experienced in allocating a suitable area of the envelope to the deposit.

In the case of G tubes, having a large bulb, the mirror is normally deposited at the valve bottom. Alternatively, the getter could be fired from a position which ensures deposition at the top of the valve, without incurring the risk of excessive heating of the deposit. In the former case a single getter will produce a deposit of an appr. size of 15-25 cm².

Similar conditions apply in the case of GT valves. Here, prompted by the good directional properties of most modern getters, industrial practice shows a marked trend towards deposition at the top of the valve. A single getter, deposited the convential way, *i.e.* at the bottom of the valve, produces a mirror area varying from 10 to 15 cm².

In recent years the method of employing two getter units simultaneously in valves of the G and GT type has become increasingly popular. The units are placed on opposite sides of the bottom region and as a result a mirror deposit very nearly double the normal size is obtained.

Finally, in the case of miniature valves, particularly the American and Rimlock valves, it is now uniform practice almost throughout the whole of the industry to fire the getter into the top of the valve. In this manner it is possible to obtain active surfaces of an area of 5-8 cm².

The Processing Characteristics of Getters

'Ideal' Requirements of the Valve Processing Engineer. The properties demanded of a good getter are many. Essentially they have to satisfy three major requirements: (*a*) They must suit the design of the valves in which they are to be used; (*b*) manipulation and firing of the getter must fit in smoothly with the general production procedure and (*c*) absorption performance of the getter deposit must ensure long operational life of the valve at the stipulated electrical characteristics.

In this article we are first of all concerned with

Table I. **Pumping Stems—Dimensions and Conductance Values**

Valve Type	*Stem External Diameter mm.*	*Wall Thickness mm.*	*Stem Length mm.*	*Stem Conductance Values cm.³/sec.*
Miniatures	3.45 — 3.9	0.6 — 0.9	56	405 — 9.4
„	3.45 — 3.9	0.6 — 0.9	106.5	22 — 9.4
„	4.06 — 4.57	0.76 — 1.04	87	36.5— 11
Kinescopes	8.86 — 9.55	1.52 — 1.77	109.32	285 — 156

Table II. **'Processing' Characteristics of Modern Getter Units**

Requirements of the Valve Processing Engineer	*Stirrup Getters*	*Coated-Ring Getters*	*Sintered-Ring Getters*
1	2	3	4
	Design Features		
(*1*) Correlation of valve geometry and Getter unit design	Obtainable only by manufacturing regularly some 100 different types	Obtainable with a minimum number of types, say, 2 standard sizes	Obtainable with a minimum number of types, say, 2 standard sizes
(*2*) Containment of the getter charge in manipulation	Good	Questionable	Good
	Typical 'Processing' Characteristics		
(*3*) Chemical stability of the getter charge in storage	Varies with the state and composition of the alloy		Good
(*4*) Chemical stability of the getter charge under exposure to air	Varies with the state and composition of the alloy		Good
(*5*) Chemical stability of the getter charge during hot liquid treatment	Varies with the state and composition of the alloy		Not affected
(*6*) Mechanical stability of the getter charge with respect to vibration	Good		Good
(*7*) Chemical stability of the getter charge in dry heat treatment	Varies with the state and composition of the alloy		Good
(*8*) Control of flashing	Pre-flashing can be avoided	Pre-flashing can be avoided	Pre-flashing can be avoided
(*9*) Low h.f. power supply	Practical, depending on shape and dimensions of the unit	Adequate in every case	Adequate in every case
(*10*) Consistency of flashed quantities	Not ensured		Good
(*11*) Minimal pressure dependence of the firing process	Not obtainable	Obtainable	Obtainable
(*12*) Moderate gas emission	Varies with the state and composition of the alloy	Not satisfactory	Satisfactory
(*13*) Avoidance of container fusion	Not ensured	Virtually safe	Virtually safe
(*14*) Avoidance of loss of solid getter material due to irregularities in firing	Not ensured		Ensured
(*15*) Two-stage evaporation	Not practical		Practical
(*16*) Directional control of getter evaporation	Lacking	Good	Good
	Performance of the Deposit		
(*17*) Consistency of deposit size and weight	Unreliable	Good	Good
(*18*) High total absorption capacity of the deposit towards all gases at all temperatures and operational conditions	Leaves much to be desired	Good	Good

the properties of the getters appertaining to Group (*b*), *i.e.* with getter problems in the sphere of the valve processing engineer. Therefore, in the analysis given below, particular emphasis is given to requirements which, if fulfilled *in toto*, would be considered ideal by the person in charge of valve production.

The various points enumerated in this analysis are not necessarily listed in the order of their importance.

Design Features

(*1*) The getter unit must be of a shape and of dimensions which fit the geometry of the valve assembly and the dimensions of the envelope.

(*2*) The method of affixing the getter unit to the valve assembly must be simple and easy to effect, avoiding deformation of the getter unit or similar mishaps which may result in the loss of getter material during handling.

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Typical 'Processing' Characteristics

(*3*) The getter material should be stable enough to facilitate storage for protracted periods provided reasonable safeguards are applied such as storage in vacuum packages or in an inert gas atmosphere.

(*4*) When withdrawn from stores and unpacked for use, the getter material should be stable enough on exposure to air, not to deteriorate for a period lasting several days or weeks.

(*5*) The getter, *in situ*, must not deteriorate during washing of the electrode assembly in hot water or alcohol, a process which is frequently carried out in order to remove traces of grease on the metal components prior to mounting the assembly in the glass envelope. Drying after washing is normally carried out by infra-red radiation.

(*6*) The getter material must be firmly located in the container of the getter unit and must not be affected by mechanical shocks and vibrations originating in the course of valve production after insertion of the unit. Any loose particles of getter material will migrate through the valve interior and cause premature failure of the valve in operation.

(*7*) The getter material must withstand heat treatment up to 500°C, *i.e.* processes such as the degassing of the valve assembly, which is carried out with the getter *in situ*. In particular, the getter must not absorb any appreciable amount of gas which would be emitted when the getter is flashed.

(*8*) Any risk of erratic and uncontrolled flashing during the process of degassing the getter itself *in situ*, should be eliminated.

(*9*) Normally getters are fired by means of an h.f. induction heating method. The power required should be low enough to exclude the danger of overheating other valve components.

(*10*) Firing of the getter should be foolproof, producing steady amounts of liberated barium. If the quantities liberated vary every time, being deficient in one case and excessive in another, uniformity of quality of the finished processed valves is impaired.

(*11*) The proper firing and activation of the getter should be largely independent of the pressure prevailing in the valve at the time. As is known, the evaporation rates of metals depend on the temperature at which evaporation is effected. The latter, in the normal event, is determined in turn by the pressure prevailing in the valve. Thus, the firing properties of the getter should be such that they overcome the effects of pressure variations within a large range.

(*12*) A further aspect of the conditions described in (*11*) is the requirement that the gas emission from the getter should be low and, above all, controlled, so as to be uniform whenever it is subjected to heat.

(*13*) Inadequate design of the getter unit may cause the container to fuse on firing. As a result, metallic particles may break loose and migrate through the valve interior, and evaporation performance may become erratic.

(*14*) If the flashing is explosive it may cause particles of unevaporated getter material to become detached from the getter unit and migrate through the interior of the valve.

(*15*) The nature of the getter material and the design of the getter unit should be such as to facilitate two-stage evaporation. This is desirable,

as it is a frequent practice to fire the getter a second time after ageing of the valve, in order to restore the operational vacuum which may have been impaired by gas emission during the ageing run.

(*16*) Proper siting of the getter deposit and a getter unit design which facilitates controlled directional evaporation is important. In the absence of the same, barium may be deposited on micas, electrodes and grids within the valve, which can give rise to serious difficulties due to loss of insulating properties, uncontrolled discharge phenomena and secondary emission occurring on the grid.

Performance of the Deposit

(*17*) The quantity of barium evaporated should always be the same both in respect to the area and to the weight of the deposit. This is imperative to ensure uniform getter deposit performance in the valves. The barium quantities required in miniature valves range from 2 to 3 mg. but in certain instances, where the gas problem is of a special nature, amounts up to 8 mg. are employed.

(*18*) The total absorption capacity of the getter deposit should be as great as possible for all types of gases under all operational and temperature conditions.

Actual Behaviour of Modern Getters in Valve Production. The analysis given in the preceding section is summarised in Table II which at the same time gives an indicative assessment of the various actual processing characteristics derived from practical experience with the three representative types of getter units discussed in this paper. In order to obtain a more complete picture of the situation the following comments are added.

Stirrup Getters

Column 2 of Table II represents the collective record of the three stirrup getters considered here, *i.e.* the Kic, the Phic and the St2 getter unit. Broadly speaking, the processing behaviour of all three stirrup getters is very much alike. However, there are some differences in all those characteristics which depend directly on the degree of stabilisation achieved by alloying the getter material proper. All three getter units are known to carry a barium-aluminium alloy as the charge but, while the material of recent St2 getters consists of a 56:44 Barium-aluminium alloy, the other two getters may carry a charge of either different proportions or of a varying crystalline state. Where such discrepancies occur in the behaviour of the three getters, a note to that effect is inserted in the table.

Allowing for the deviations in the behaviour just mentioned, the table shows that the stirrup getter as a type is falling short of the 'ideal' requirements of the valve processing engineer.

Take Requirement No. 1, for instance. It is estimated that the variety of stirrup getters available on the market to meet the needs of the valve industry approaches 100, differentiated by shape, size and barium content of the unit. This condition alone is a clear verdict against the stirrup getter.

More important still are the deficiences in respect to Nos. 9, 10 and 13. Generally speaking, firing of the getter is foolproof and this constitutes a substantial advantage over older types of getters but evaporation is somewhat erratic. This latter condition originates from the method employed normally for firing, *i.e.* the h.f. induction method. Ordinarily, the getter bar (the container) is made from iron and the looped wire support is made from nickel. Consequently, if a powerful h.f. supply is used, the getter bar will heat up more rapidly than the supporting bracket and even if the power is only applied for a short period the central portion of the bar may fuse. Alternatively a weak* h.f. supply, left on for a comparatively long period, will produce a temperature equilibrium all along the container but by that time the supporting bracket is overheated with the attendant result of barium vapours rising from the ends of the bar rather than all along its length. In practice, the period elapsing between initiation of the h.f. supply and inception of the evaporation of barium varies from 2 to 15 secs.

Generally, the firing conditions stipulated by the getter manufacturer (normally varying from 4 to 6 secs.) represent a compromise between the two extremes just mentioned and are determined by trial and error. However, even small deviations from the

stipulated conditions may render the evaporation critical.

It is implied in the foregoing remarks that the directional control of the evaporation in stirrup getter units is poor. In many instances it is virtually non existent, especially, if the getter bar is overheated and part of it starts fusing.

Finally, let us turn to Requirement No. 11. The evaporation of the alloys employed in the stirrup getters considered is an endothermic process.* Consequently, temperature and rate of the evaporation depends invariably on the pressure prevailing in the valve at the moment of firing. In a bad vacuum, *i.e.* at pressures ranging from, say, 0.1 to 1 mm.Hg the evaporation temperature may reach that of the melting point of the getter container material. This is a notable disadvantage of this type of getter keenly felt in industry. The problem has been taken care of with success in the development of the ring getters which will be discussed below and this is one of the reasons why the latter represent considerable progress in getter unit development.

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Ring Getters

On entering the discussion of the processing characteristics of ring getters the author should mention that his experience with Telefunken coated-ring getters is limited and this accounts for the blanks shown in Column 3 of Table II. Even so, assessing the values of the coated-ring getter by the restricted information available only, the table demonstrates clearly that the ring getter as a type has features in its processing behaviour, inherently superior to those of the stirrup getter. Compare, in particular, the assessments shown against Requirement Nos. 1, 9, 11, 13 and 16.

Typical features inherent in the ring design of getter units are improved directional control of evaporation, reduced h.f. power requirements and reduction of the variety of dimensions of ring getter units necessary to satisfy the diversified needs of modern miniature valve manufacture. In fact, four standard sizes would virtually cover the whole range of existing valve types.

Table III gives five representative sizes in which the sintered-ring getter unit is made available. Fig. 9 illustrates the effectiveness of the directional control of the evaporation obtainable with a ring-getter: The border of the ring getter deposit shows perfect regularity. In the case of a circular cross-section the combination of ring shape and low h.f. power has the additional benefit of eliminating the development of hot points during firing.

Table III. **Sizes and Barium Contents of Sintered Ring Getters for Receiving Valves**

Type of Valve	*Designation*	*Outer Diameter mm.*	*Barium Content mg.*
Subminiatures	St14/0/5	5	1
Special miniatures	St14/0/9.5	9.5	2.5
Standard 7-pin miniatures	St14/0/11	11	3
Standard 9-pin miniatures	St14/0/13	13	4
Power miniatures	St14/0/13/r	13	8

Finally, as indicated before, the ring getters carry a charge comprising a modified barium alloy prepared with the intention of causing the evaporation to take the form of an exothermic process. This is a new departure as far as getter material composition is concerned and constitutes a major advance in the direction of making the evaporation of the getter material independent of the prevailing pressure in the valve, thus ensuring that flashing occurs every time at the desired temperature.

The two ring getters considered here seem to differ substantially only in two respects see Requirements Nos. 2 and 12.

In the case of the Telefunken unit the getter charge is secured to the ring by means of a bonding medium. This method of applying the charge to the ring involves the risk that particles of the getter material may detach themselves during manipulation of the unit and may be trapped in the valve. Another drawback is the considerable evolution

* A slight exothermic effect may be present caused by reaction of the aluminium in the alloy with the iron of the container.

of gases caused by the decomposition of the bonding agent during firing of the getter.

In the case of the S.A.E.S. getter, the charge is applied to the ring by a sintering process. This obviates the need for the use of a bonding material, and the absence of the latter disposes of the gassing problem. In addition, it appears that sintering provides a firmer bond and loss of material during handling is minimised.

The performance characteristics of the deposits obtained from the coated-ring getter and the sintered-ring getter are very similar and will be discussed in the final section.

The Testing of Getters

In order to make certain that the getters have uniform processing characteristics and are of consistent quality it is advisable to institute routine testing of samples taken from each batch before it is used in valve production. Preferably, such tests should be carried out on the premises of the getter manufacturer before the getter units are packed and dispatched.

In the works of the author samples of each production batch are checked with regard to the following properties:

	See Requirement No:
(*a*) Barium content of the charge	—
(*b*) Gas emission during flashing	*12*
(*c*) Barium yield	*17*
(*d*) Performance characteristics of the deposit	*18*
(*e*) Stability of the getter alloy	*4*
(*f*) Adhesion of the getter material to the ring	*2*
(*g*) Firing characteristics (in the case of stirrup getters only)	*10*

The testing of the properties (*a*), (*b*), (*c*) and (*d*) is carried out on an apparatus consisting essentially of a vacuum manifold which can revolve and has ten outlets, to each of which a small glass bulb containing the sample to be tested is joined. The manifold is evacuated by a diffusion pump unit and a valve facilitating flow adjustment is inserted in the pumping line. The pressure is read on a Penning-type vacuum gauge. The size of the sample containers employed in the tests varies in accordance with the type of getter to be tested.

As a first step, after loading the containers with the samples, the containers are evacuated. Next, the manifold is rotated in order to position one of the ten containers in the immediate proximity of the high frequency coil, fitted to the apparatus for the purpose of firing the getter. At this stage the first pressure reading is taken, *i.e.* the value of the pressure in the manifold immediately prior to firing. The reading is recorded in a graph, see point *A* of Fig. 10. The getter is then fired. In the process gas emission takes place increasing the pressure in the container. The maximum pressure reached during firing is observed and recorded, see point *B* in graph Fig. 10. Subsequently, the pressure falls again and the pressure reading recorded at point *C* represents the pressure prevailing in the vessel after a certain predetermined period of observation. The size of the area under the curve obtained by drawing a line through the points *A*, *B* and *C* gives an indication of the volume of gas liberated by the getter during flashing.

This procedure is repeated for the remaining nine samples, charged to the testing apparatus initially. As long as the samples investigated in one run are of the same type, the readings *A*, *B* and *C* should be of roughly equal magnitude. Any reject is easily spotted by this method, see the dotted line in Fig. 10.

While this test is essentially designed to check the gas emission of the getter unit, it is at the same time a measure of the barium content and barium yield, as long as the weight of the getter unit tested is determined before and after flashing. Naturally, as the characteristics of the getter recorded in this test are at the same time a function of the stability of the getter alloy comprising the charge, the test just described furnishes also some rough indication of the quality of the getter material in this respect. However, it is advisable to test alloy stability in a separate run. The same equipment can be used but the getter to be tested should be exposed to air for a period of at least six months or,

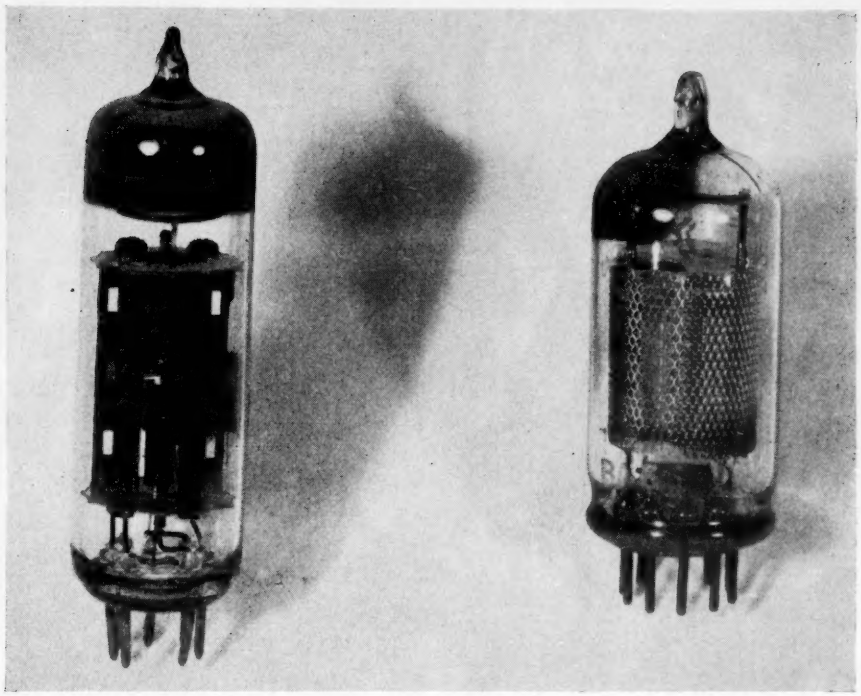

Fig. 9. Miniature Valves with barium microns evaporated (*a*) from a ring getter and (*b*) from a conventional 100p getter.

(*a*) (*b*)

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alternatively, should be kept immersed in water for some time.

Finally, the potential loss of getter material during manipulation is determined by immersing the samples in petroleum ether and exposing them to short bursts of ultra-sonic waves, and the firing properties of stirrup getters are checked by measuring the temperatures obtained and the times elapsed between the initiation of a given h.f. supply and the inception of barium evaporation on one hand, and complete burn-out of the getter on the other hand.

The absorption characteristics of the deposit are checked in an apparatus, details of which have been given in a previous contribution.[1]

SOME PERFORMANCE CHARACTERISTICS OF MODERN GETTERS

This article deals essentially with the requirements of the valve processing engineer and performance characteristics of the mirror deposits in

Fig. 10. Typical Record of a test of gas emission on a batch of 10 getters.

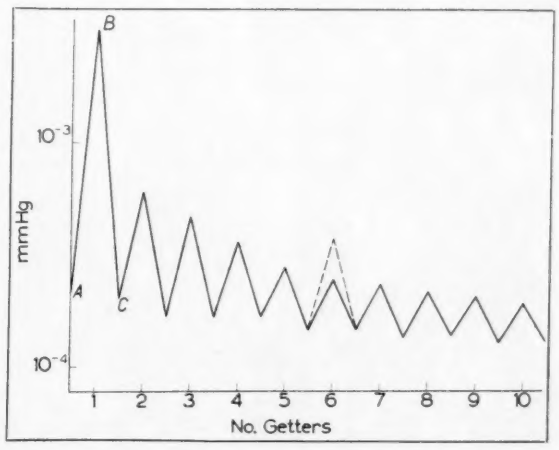
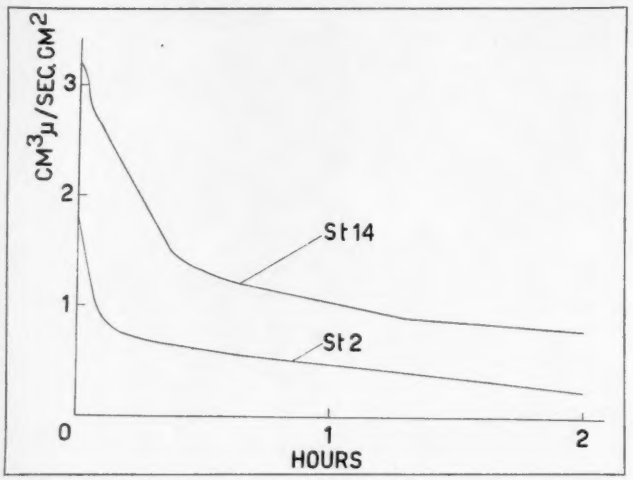
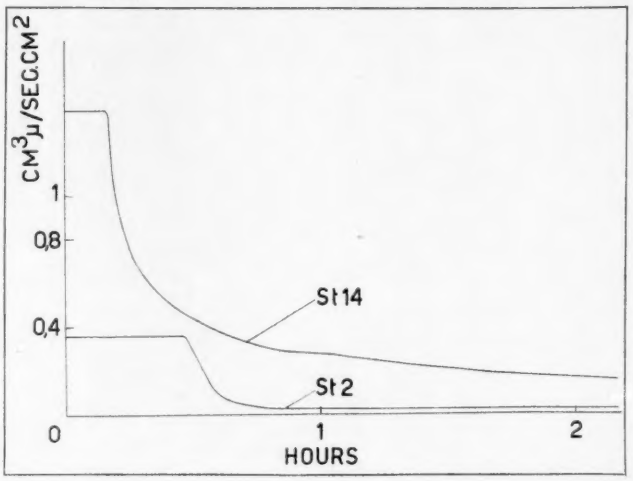


Fig. 11. Values of the Absorption Capacity of 50:50 Ba/al Getters and New Alloys of SAES Ring Getters Determined for Various Gases. Mirror Area: 1 cm^2.

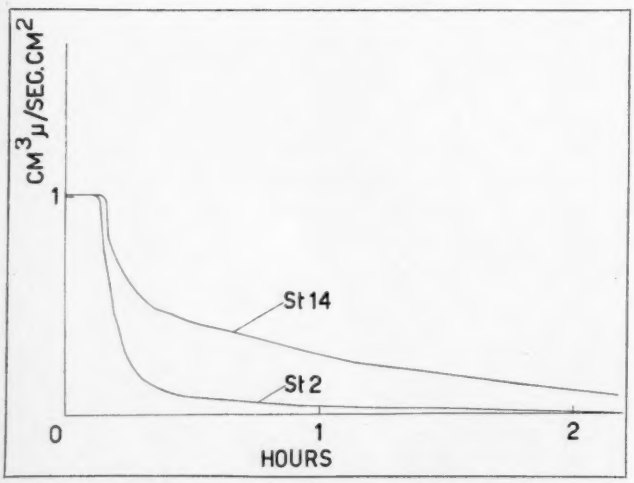
(*a*) Hydrogen; Pg = 3×10^{-4} mm. Hg.



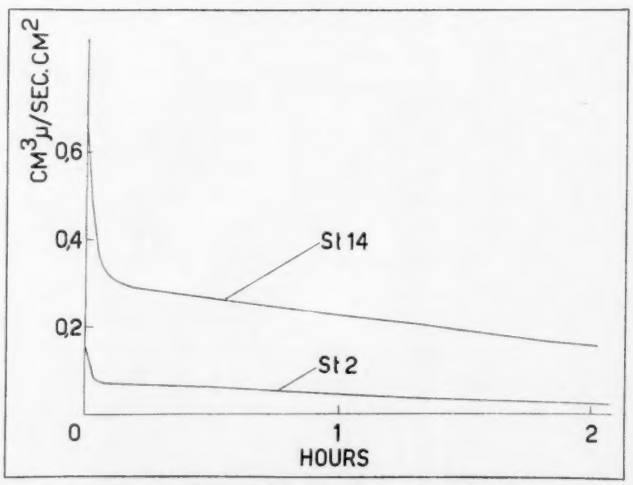
(*b*) Carbon Dioxide. Pg = 9×10^{-6} mm. Hg.



(*c*) Carbon Monoxide. Pg = 9×10^{-6} mm. Hg.



(*d*) Nitrogen. Pg = 3×10^{-4} mm. Hg.



terms of total absorption capacity are not necessarily a concern of the person in charge of production. However, the author feels that this survey would not be complete without brief remarks being added on the improved performance of deposits obtained from ring getters, *i.e.* on the qualities, called for under Requirements Nos. 17 and 18. As indicated before both the coated and the sintered-ring getter, have broadly speaking equally satisfactory features with regard to these requirements and, as the author is more fully conversant with the performance of sintered-ring getters, he may be permitted to substantiate these claims by referring to the sintered-ring getter performance, in particular.

Fig. 11 *a-d* shows graphs depicting the total absorption capacity of a sintered-ring getter St14/0 as compared with a stirrup getter carrying a 56:44 barium-aluminium alloy, type St2. As can be seen hydrogen and carbon dioxide are taken up in quantities five times as large as those taken up by the stirrup getter. Carbon monoxide absorption shows only a threefold increase but the decay of the capacity of the ring getter for that gas proceeds at an appreciably lower rate than for other gases.

***Table IV.* Total Absorption Capacity of Stirrup Getters and Sintered-Ring Getters at Valve Operational Temperature**

Gases	*Quantity Absorbed*	
	Stirrup Getters	*Sintered-Ring Getters*
Oxygen	50 lμ/mg.	50 lμ/mg.
Moisture	35 lμ/mg.	61 lμ/mg.
Hydrogen	4.48 lμ/cm.^{2}	13 lμ/cm.^{2}
Carbon dioxide	0.60 lμ/cm.^{2}	1.8 lμ/cm.^{2}
Carbon monoxide	0.72 lμ/cm.^{2}	3.7 lμ/cm.^{2}
Nitrogen	0.33 lμ/cm.^{2}	2.25 lμ/cm.^{2}
Dry air	0.64 lμ/cm.^{2}	2.6 lμ/cm.^{2}

The most important improvement, however, is the absorption capacity towards nitrogen, which is seven times that of the stirrup getter. Table IV gives an over-all picture of the situation. The practical benefits of the improved performance of the ring getters are bound to express themselves in terms of extended operational life of the valve and the author understands that evidence of this has already been established in industry.

It must be admitted, at least on the part of the works represented by the author, that the degree of improvement obtained with ring getters is somewhat unexpected and its causes are still obscure. In the case of the S.A.E.S. ring getters the flashed barium vapours carry with them certain metallic additions and it is believed that these additions lead to the formation of impurity centres within the deposit, the presence of these impurity centres being ultimately responsible for the raised activity of the deposit. More information on this subject will be made available as investigation of this problem proceeds.

CONCLUSIONS

In the above paper the author presents information on gettering technique, taking particularly into account latest getter designs and practical requirements in modern valve manufacture.

The very early phases of getter development discussed in the introductory section, *i.e.* the period prior to World War II, has not been treated extensively. Littmann's book and two articles which appeared in 'Light Metals' give considerable information on initial developments, covering the period up to 1944. Equally informative is the article by Espe, Knoll and Wilder[1], quoted previously.

The most significant trend in modern thermionic valve design is the evolution of the miniature type. Miniature valves are estimated to form some 95% of all receiving valves produced today. This trend had a considerable effect on getter development. The high rate of miniature valve production, their compact shapes, the elevated operational temperatures, the restricted size of the areas available in the valve for getter deposition and, last but not least, the close proximity of the deposit to the electrodes are all factors imposing on the getter the most exacting performance requirements.

The present article is intended to show, how the getter specialist responded to the challenge. Haphazard experiment, and the application of merely empiric experience and skill of the individual have gradually been superseded by methodic

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investigations and research conducted collectively, leading eventually to the formation of a properly equipped industry in its own right. This industry, although still young, has already proved its ability of meeting the problems as they present themselves, see the ring getter. Other avenues of getter research, such as performance characteristics and absorption mechanisms of getter materials with respect to various gases and gas mixtures, have been discussed in previous contributions and will be referred to again by the author in future papers.

In conclusion, the author wishes to express his thanks for many valuable suggestions received from Mr. W. Steckelmacher and Mr. S. Price of Edwards High Vacuum Ltd., while preparing this paper.

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VACUUM METALLURGY IN THE UNITED STATES

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Summary

THE AUTHOR DISCUSSES the various forms of vacuum processing existent in the metallurgical industry today. Detailed attention is given to all aspects of vacuum induction melting, such as furnace design, pumping plant, refractories employed, typical reactions leading to the purification of the processed material and properties of the product. Similar information is given on the consumable electrode melting method. Present-day U.S. plant capacity for the former process is estimated at an annual throughput of 5,000 tons and for the latter process at 12,000 tons. The article concludes with a brief mention of vacuum sintering and the Bochumer Verein process.

Sommaire

L'AUTEUR EXPOSE les différentes formes de traitements sous vide actuellement employés dans l'Industry Métallurgique. Les informations détaillés sont données sur tous les problèmes dans la fusion sous vide par induction, tels que, constructions de fours, groupes de pompage, réfractaires employés, réactions permettant purification du produit traité et ses propriétés. Les informations semblables sont données sur la méthode de fusion par électrode consommable. La capacité de l'équipement actuel aux Etats Unis pour la méthode par induction est éstimée à 5,000 tonnes par an et 12,000 tonnes pour la méthode à électrode consommable. L'auteur termine en mentionnant brièvement le frittage sous vide et le procédé de Bochumer Verein.

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INTRODUCTION

IN THE PAST TEN YEARS vacuum metallurgy in the United States has undergone extensive development and several processes have grown from the laboratory to fully fledged production operations. The most notable of these are:—

(*1*) Vacuum induction melting of steels, high-temperature alloys, high-purity metals, non-ferrous alloys, structural and reactive materials for the atomic energy programme,

(*2*) Consumable electrode melting of titanium and zirconium[1] for aircraft and atomic energy applications,

(*3*) The application of the same process to the production of some high-temperature alloys, refractory metals and steels,

(*4*) The process for producing 'Simplex' low carbon ferrochrome.

(*5*) Vacuum sintering of mixed carbides, and

(*6*) Stream degassing of steel.

Although the advantages of vacuum processing had been apparent for many years, the lack of adequate pumps and large-scale vacuum equipment made costs prohibitive for production operations.

The early work of Dr. W. Rohn[2] at Heraeus Vakuumschmelze in Germany during the first World War and the early 1920's demonstrated improved quality for thermocouple and resistance alloys, beryllium-copper and soft magnetic alloys, when melted in vacuum, but the inefficiency of equipment made the economics of the process questionable.

With the inception of the atomic energy programme in the United States, it became obvious that metals and alloys of hitherto unattainable purity were essential and that vacuum melting represented

* MS. received July, 1957.

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the only known means of achieving the required quality. Since cost was of secondary importance, an intensive development programme was undertaken to develop large-scale equipment. This work was eminently successful and much of the technological advancement achieved as a result of this work was applied to the manufacture of equipment for other processes.

National Research Corporation, Cambridge, Mass., one of the participants in the early developments, did a great deal of laboratory-scale melting in 30-pound furnaces and built a 300-pound unit in 1949 as the first phase of a programme to develop commercial markets for vacuum melted metals and alloys. During the first two years of operation, the versatility of the equipment was demonstrated by the successful production of high-purity metals, such as iron, nickel and copper, and the manufacture of a wide variety of steels and non-ferrous alloys of all types.

Evaluation of early steel heats demonstrated that the low gas content and relative freedom from non-metallic inclusions greatly improved the fatigue life of ball bearing steels, such as SAE 52100[3], and a substantial demand for steel for aircraft bearings followed, see Fig. 1. Evaluation of high-temperature alloys for jet engine buckets and blades demonstrated greatly enhanced high-temperature properties and the demand for this type of material far exceeded available capacity. The insistence of engine builders for these materials resulted in a rapid expansion of facilities, and to-day there are six established producers and an equal number starting to operate production facilities. In spite of this tremendous increase in capacity and aside from cost, the major factor preventing wide application of the product is the complete inadequacy of facilities to meet the demand. Equipment is improving and, as capacity increases, operating costs are reduced. It appears evident that more diversified applications of vacuum melted materials will result when facilities more nearly match the military aircraft demands.

In 1948 total production of vacuum induction melted material probably amounted to 5 to 10 tons per year, exclusive of atomic energy production. Although accurate production figures are not available, the following estimates of capacity indicate the growth during the past ten years:—

Vacuum Induction Melting	4,000-5,000 tons/year
Titanium Melting	30,000 tons/year
Consumable Electrode Melting (High Temperature Alloys, Refractory Metals and Steels)	10,000-12,000 tons/year

Titanium melting capacity currently appears to be adequate, but expansion planned and under way should more than double the capacity for other types of melting within the next year.

Wide application of the product of both vacuum induction and consumable electrode melting furnaces is anticipated. Each process has advantages and a description of each follows.

INDUCTION MELTING

The Furnace

Present equipment ranges from 350 to 3,000-pound capacity, with nearly all new furnaces being built in the 2,000-3,000 pound size. Furnaces of 5,000- and even 10,000-pound capacity have been studied but to date none have actually been built. The furnace shown in Fig. 2 has been in operation at Vacuum Metals Corporation for nearly two years[4]. Melts of approximately 3,000 pounds are made regularly. Although production furnace designs vary considerably, this unit incorporates the basic design concepts considered essential for commercial operation. The furnace is designed to operate continuously without breaking the vacuum in the main chambers.

The crucible is filled with melting stock from a charging chamber through a vacuum lock. Materials can be charged in any desired sequence at any time during the cycle. Moulds enter the furnace and ingots are removed by means of a mould lock. The heat can be poured into one or more moulds, depending upon the application, and ingots can be removed while red-hot or allowed to cool in vacuum as desired. Small vacuum locks permit taking samples from the bath, making very small alloy additions, and taking temperature measurements with immersion thermo-

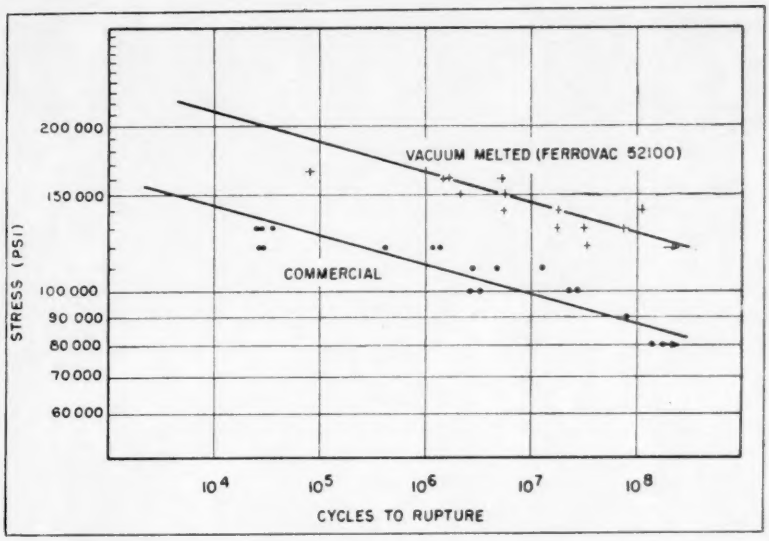

Fig. 1. Rotating beam fatigue behaviour of *FERROVAC 52100 and commercial 52100.

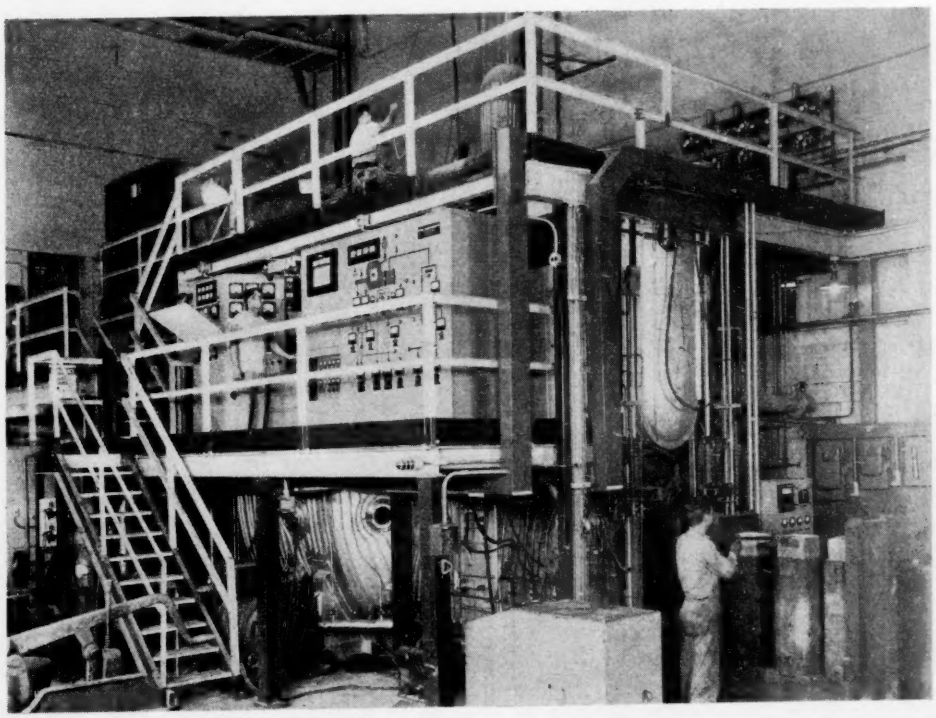

Fig. 2. Vacuum Metals Corporation 3,000 lb. induction furnace.

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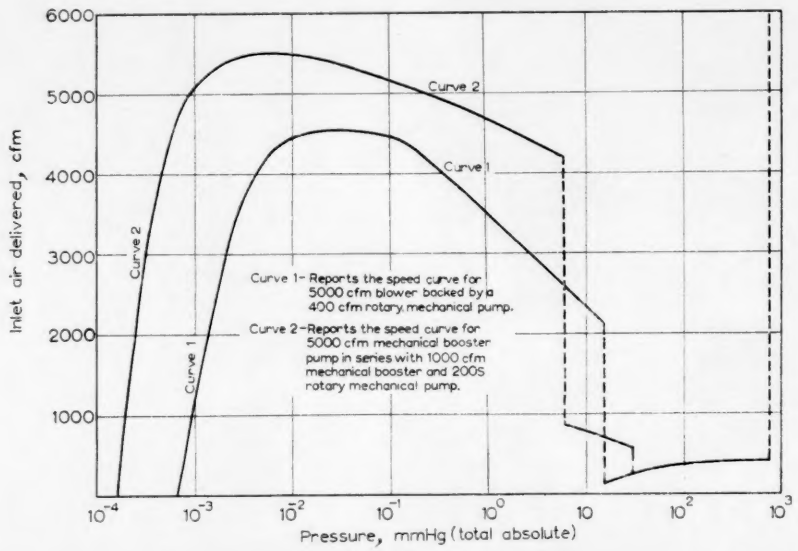

Fig. 3. Comparison of speed curves of single-stage and multi-stage mechanical booster pumps.

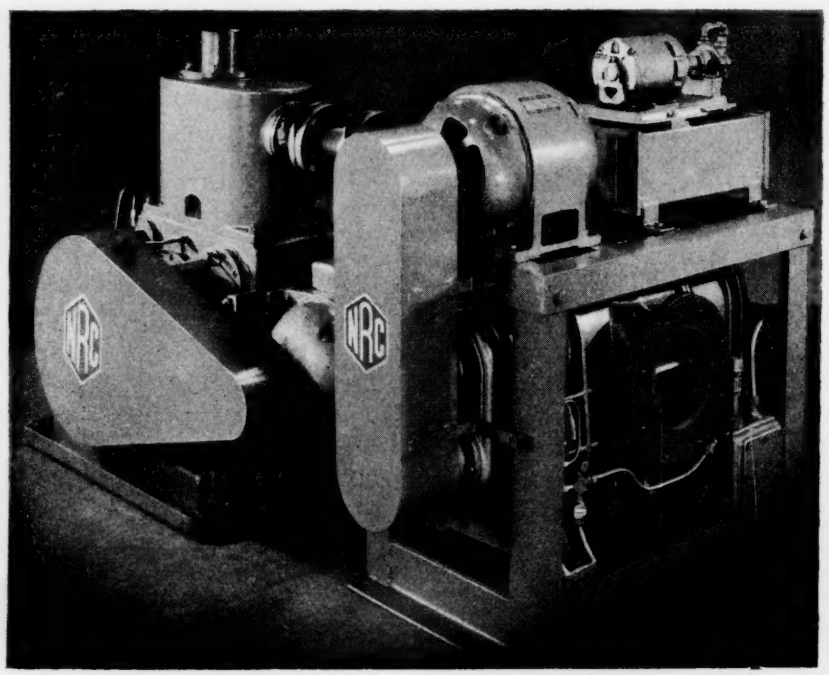

Fig. 4 5,000 cfm mechanical booster pump.

by Courtesy of National Research Equipment Corp.

couples.

The furnace is normally operated 24 hours per day and is opened only for mechanical repairs and changing coil assemblies.

Electrical Data. Power is supplied from a 700 kW, 960 c.p.s., 800 V motor-generator set. This is the highest voltage used in production to-day and has proved to be entirely satisfactory. Laboratory furnaces normally operate at 200 V or less, with bare copper coils. At approximately 220 V, arcing becomes a problem in vacuum and insulation of coils becomes mandatory. Since arcs can travel a distance of several feet in vacuum, it is necessary to insulate all parts that are of more than 220 V above ground potential. Although units of this size can be operated satisfactorily at 400-600 V, the higher voltage was chosen in preparation for building larger furnaces which would require these higher voltages, if conductor sizes and circulating currents were to be kept within practical limits. It has been demonstrated that electrical designs for larger units are practical.

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Power and water are delivered to the coil through a rigid co-axial tube that rotates with the coil assembly during pouring. Other large furnaces use flexible rubber-covered power and water leads or flexible water leads with electrical contacts on which the coil rests during the melting cycle. The first two methods currently appear to be the most satisfactory and the choice depends largely upon cost for a particular furnace design.

Vacuum Plant. Operating pressures of 1 to 10 micron Hg absolute are attainable. This furnace utilises rotary mechanical pumps, mechanical blowers (Roots-type) and oil diffusion pumps. Some other production furnaces utilise pumps that are a combination of oil ejectors and oil diffusion pumps, backed by mechanical pumps.

Both types have advantages and the choice depends upon the particular application. By utilising mechanical blowers, operating pressures of 1 to 10 micron Hg can be achieved. A further improvement in pumping speed at low pressures can be achieved by operating two or three blowers in series, see Figs. 3 & 4. This type of installation is expensive for a given capacity in the 1 to 10 micron Hg range but has a high capacity well up into the millimetre range, *i.e.* up to approximately 15 mm. Hg. Single units are available in the mechanical blower range with speeds up to 13,000 cfm. The upper pressure limit can be raised by increasing the motor size but in most cases pumping capacity above this pressure is provided more economically by conventional mechanical rotary pumps.

The oil ejector pump has a very high capacity in the range of 1 to 10 micron Hg, but falls off rapidly above this pressure. One ejector-blower unit has a peak speed of 40,000 cfm (18,000 l./s.), see Figs. 5 & 6. The use of several units of either type in parallel is common and construction of extremely large pieces of equipment operating in the low micron range is entirely practical. Steam ejectors, while not commonly used for vacuum melting operations, are becoming more highly developed. Five- and six-stage units are in use and these are capable of achieving pressures well down in the micron range. They represent a low equipment cost for large systems and are competitive if low-cost steam is available. They are commonly used for obtaining pressure of 50-100 micron Hg in extremely large systems and may soon become common for vacuum melting furnaces and other equipment operating at pressures below 10 micron Hg. They hold a great deal of promise for use on really large vacuum equipment since units having tremendous pumping capacity can be manufactured readily. They appear to require very little maintenance.

Furnace Linings. Nearly all large furnaces now utilise rammed refractory linings. The refractory grain is normally rammed dry in back of a reinforced steel form or a graphite plug of the desired shape. The steel form is melted away as part of the charge for the first melt or 'sinter heat', while the graphite plug is used as an inductor to heat the lining. It is then cooled and removed before starting the first heat. The most commonly used materials are magnesia-alumina refractories containing 60-80% magnesia, with the balance mainly alumina. Bonds, such as clay, are kept at a minimum since they form low-melting phases that may dissolve in the bath. In

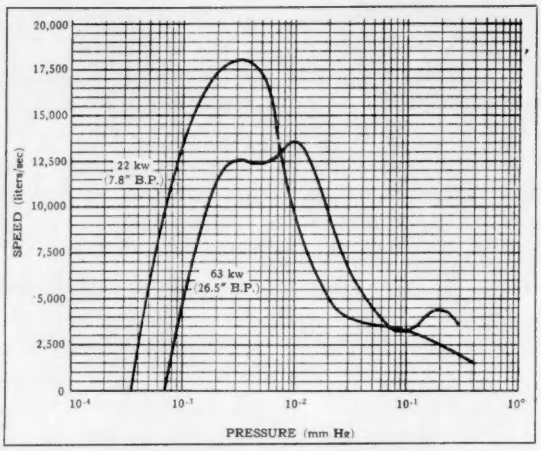

Fig. 5. Performance of oil diffusion ejector pump. Pump fluid—Convaclor-8; water cooling rate—25 gal./min.; water inlet temperature—20°C; mechanical pump—229 l./sec.

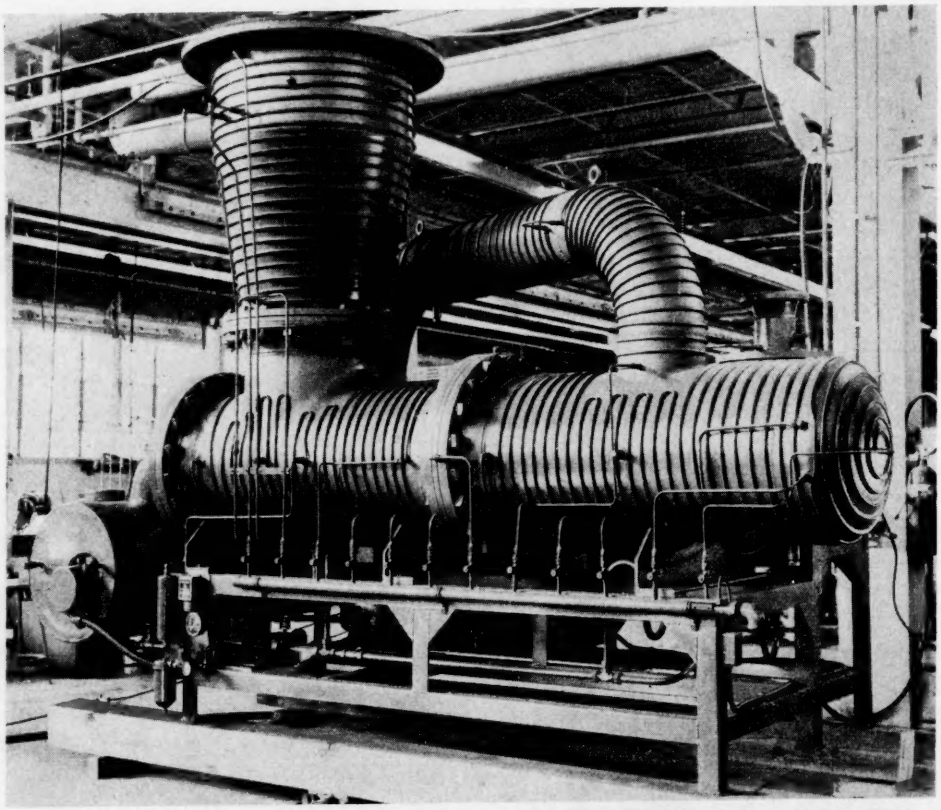

Fig. 6 (Below). Oil diffusion ejector pump—type KS16000.

by Courtesy of Consolidated Electrodynamics Corp., Rochester Division.

addition, these materials lower the sintering temperature of the refractory. Since vacuum melting cycles normally include extended periods of purification in the molten state, the linings tend to sinter more deeply than in air-melting furnaces where cycles are very short. Lining failure commonly occurs as a result of the lining sintering all the way back to the coil and then developing cracks throughout the thickness. Erosion or chemical attack of the linings does not normally represent a problem and attempts have been made to utilise materials having a higher sintering temperature, such as high-purity magnesia or zirconia. Although promising, these materials are not widely used at present in large furnaces.

The Method

Vacuum melted alloys show improved properties essentially for the reason of low gas content, relative freedom from non-metallic inclusions, close composition control, and the near elimination of trace impurities[5]. Slags are not normally used for purification or protection.

The five major reactions commonly used for purification during vacuum melting are:—

(*1*) Simple degassing by reduction in solubility,
(*2*) Vaporisation of volatile impurities,
(*3*) Dissociation of gas-metal compounds,
(*4*) Reduction of gas-metal compounds and elimination of dissolved gas by carbon or hydrogen and
(5) Reaction of carbon or hydrogen with refractories.

A schematic representation of these reactions is shown in Fig. 7.

Remarks on Purification. In many instances it is more economical to purchase high purity melting stock than to attempt too much purification in the vacuum furnace. High gas content in melting stock is usually undesirable but less harmful than the presence of other impurities that require long purification cycles. Probably the most harmful single element is sulphur, since it is difficult to reduce and extremely harmful to physical properties. Reduction by means of bath additions of metal oxides (Na_2O, etc.) has been reported, but this practice has not generally been shown to be effective. Examination of atmospheres above the bath by means of a mass spectrometer[6] fails to show the formation of sulphur dioxide or hydrogen sulphide during melting and purifying cycles. Through careful selection of melting stock and revert scrap, the sulphur level of vacuum melted steels is held in the range of 0.004/0.007% quite consistently.

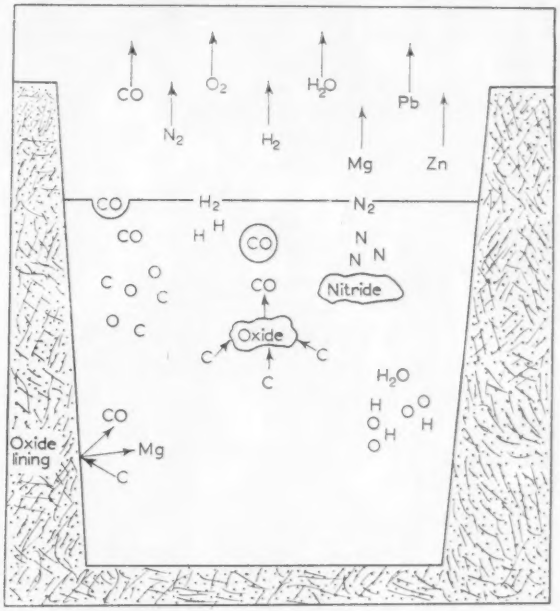

Fig. 7. The melt under vacuum.

By far the most important reaction in vacuum induction melting is

$$C+O \rightleftarrows CO\ (gas)$$

The reduction of metal oxides proceeds quite rapidly and, since the reduced pressure shifts the equilibrium to the right favouring the gaseous product, and since the gas is constantly removed, reduction is quite complete. This reaction is readily controlled in most cases by measuring the rate of CO-evolution from the bath. Obviously, it proceeds most rapidly in the case of relatively high carbon alloys, since there is always a large excess of one reactant. In the case of high-purity iron, a carbon

addition slightly in excess of stoichiometric ratio is added. After removal of oxygen from the melt, the excess carbon reacts with the MgO-refractory producing CO which is pumped off, and metallic magnesium which evaporates and is recondensed elsewhere in the system. Since this reaction proceeds very slowly at low carbon concentrations, an effort is made to keep the excess carbon at a minimum. Typical vacuum fusion analyses of high purity iron and a high carbon steel (SAE 52100) are shown in Table I.

Table I. Typical Analysis of Purified Metals

Gas	*High-Purity Iron*	*SAE 52100*
Carbon	0.005 %	1.00 %
Oxygen	0.010 %	0.0002%
Nitrogen	0.0003%	0.0004%

Similar reduction of oxygen can be achieved with hydrogen[7]. However, in most cases the problems involved in achieving intimate contact between the gas and a large portion of the bath at any one time seriously retard the reaction rate. In essentially all cases, carbon has proved to be a more satisfactory reducing agent for production operations.

Remarks on General Practice. The general melting practice for most materials consists of melting the basic charge under vacuum and completely deoxidising the bath before adding those alloying elements which form stable oxides or nitrides. Metals having high vapour pressures are bath temperature, such as manganese or magnesium, are added late in the cycle, and, if desired, evaporation may be retarded by adding a partial pressure of an inert gas, usually argon. Normal metal recovery in terms of furnace charge to ingot weight poured closely approaches 100% since no metal is oxidised to form dross or slag. This was one of the reasons for early interest in beryllium-copper production since normal air melting results in an oxidation loss of approximately 10% of the beryllium charged as 4% BeCu master alloy. In addition, the resulting ingots possessed improved hot-working characteristics that resulted in higher yields and improved properties.

The Product

Evaluation of a wide variety of alloys has indicated a number of advantages for the process. Some of the more important ones are:—

(1) Low residual gas content,
(2) Relative freedom from metallic impurities,
(3) Relative freedom from non-metallic inclusions,
(4) Improved workability, both hot and cold, and
(5) A high degree of uniformity from heat to heat.

As a result of the above characteristics, many room-temperature and elevated-temperature properties show marked improvement over air-melted materials. Below, some typical applications utilising the above advantages are given.

Alloys for Electronic Applications. The emissivity of cathode nickel-alloys is greatly affected by minute quantities of metallic trace elements and minor variations in chemistry. Vacuum melted materials have demonstrated more consistent emission characteristics. All metals used within the vacuum tube envelope are a source of gas at operating temperatures, and the use of nearly gas-free vacuum melted materials greatly reduces the length of bake-out cycles prior to sealing the tubes and improves the 'shelf life' of tubes, especially power tubes, such as magnetrons and hydrogen thyratrons that operate at unusually high temperatures. In addition to nickel-alloys, the materials that have been used in this connection have been pure copper, pure iron, stainless steel and glass-to-metal sealing alloys of the iron-nickel-cobalt type.

High Temperature Alloys. The major portion of the available vacuum melting capacity is currently involved in the production of this type of material and, in the case of more highly alloyed materials, such as the precipitation-hardening nickel-base materials (M-252 and Waspaloy, etc.), vacuum melting has almost completely replaced air melting. These alloys are basically expensive to produce and difficult to fabricate, and the adoption of vacuum melting has improved the workability to such an extent that overall production costs are lower than for air melted material. In addition, a marked improvement in physical properties has been achieved. In

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some instances this has enabled engine builders to increase operating temperatures significantly without reducing operating stress levels. A comparison of properties between air melted and vacuum melted Waspaloy is shown in Fig. 8. The curve shown for S-816 indicates the best material available prior to the emergence of production vacuum melting facilities.

Recent studies have demonstrated that much of the improvement in the precipitation-hardening type of high-temperature alloys has been achieved by reducing the level of manganese and silicon[8] and raising the total amount of the hardening elements, titanium and aluminium, since vacuum melting permitted this without serious loss of ductility[9]. This is due to the fact that oxygen and nitrogen have been effectively removed prior to the alloy addition, and they have no opportunity to form the harmful carbo-nitrides or cyano-nitrides. A more recent development[10] indicates that a further marked improvement in stress-rupture life and ductility can be achieved through the addition of boron in the range of 0.005/0.01% and zirconium in the range of 0.05/0.10%. It was noted that small amounts of boron were sometimes picked up from the crucible refractory[11] and that the effect upon the high temperature properties was pronounced. By controlling both boron and zirconium within narrow limits, the scatter in physical properties is also greatly reduced. Perhaps even more important than the improvement achieved in existing alloys is the promise that vacuum melting gives a means of producing new malleable alloys containing larger amounts of reactive metals and having greatly improved high temperature properties. The close control available permits a more careful evaluation of the effect of minor changes of chemistry upon the properties of many alloys than has heretofore been available. Metallurgists now have a new tool with which to make truly significant developments.

Steels. To date nearly every material melted under vacuum has shown an improvement in one or more respects. Steels generally show an improvement in fatigue strength, endurance limit and transverse properties. Typical properties for Ferrovac* 4340 (vacuum melted) are shown below.

Table II compares the mechanical properties in the longitudinal and transverse directions (reduction ratio 5 : 1, smooth tensile bar specimens standard 0.505 inch diameter). Ferrovac 4340 exhibits high transverse ductility, and there is very little tendency for this vacuum melted alloy to have directional properties.

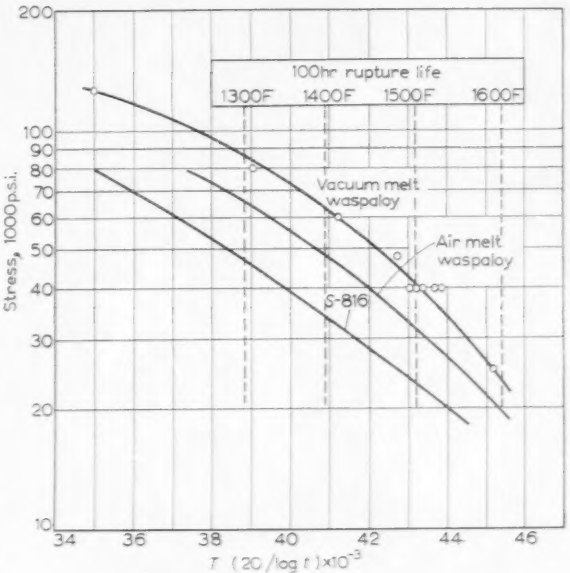

Fig. 8. Comparison of 100 hour rupture life for air-melted and vacuum-melted WASPALOY and air-melted S-816.

Fig. 9 compares the tensile strengths in the longitudinal and transverse directions using smooth and notched tensile specimens. Ferrovac 4340 has a high notched tensile strength in either direction.

Table III shows the effect of tempering temperature on V-notch Charpy impact of Ferrovac 4340. All specimens were austenitised at 1,550°F and quenched in oil.

In Fig. 10, S-N curves are plotted indicating the fatigue properties of Ferrovac 4340 and air-melted 4340. There is a significant increase in the endurance limit of Ferrovac 4340 over air-melted material at the same strength level. Ferrovac 4340 is essenti-

* Vacuum Metals Corporation.

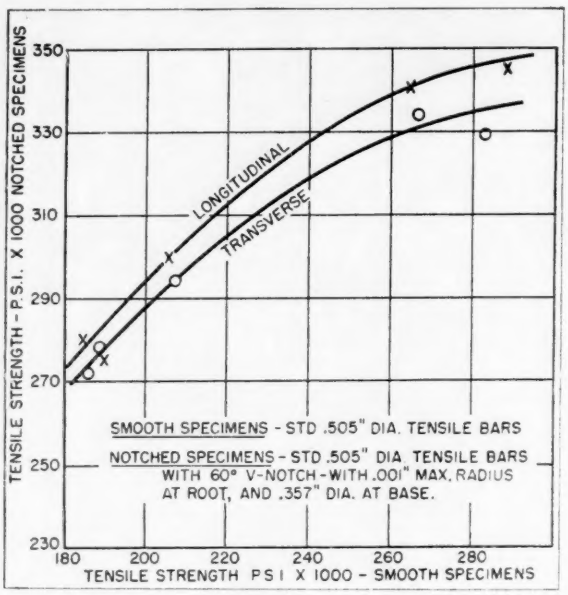

Fig. 9. Tensile properties of FERROVAC 4340.

Direction	*Tensile Strength* *p.s.i.*	*Yield Strength 0.2% Offset* *p.s.i.*	*Elongation* %	*Reduction of Area* %
Longitudinal	185,000	166,000	16	60
Transverse	185,000	170,000	12	47
Longitudinal	205,000	184,000	13	53
Transverse	207,000	189,000	13	49
Longitudinal	235,000	202,000	13	52
Transverse	239,000	205,000	15	52
Longitudinal	285,000	215,000	12	41
Transverse	287,000	222,000	10.5	40

Table II (Above). Transverse Mechanical Properties of FERROVAC 4340.

Fig. 10. Fatigue strength of FERROVAC 4340.

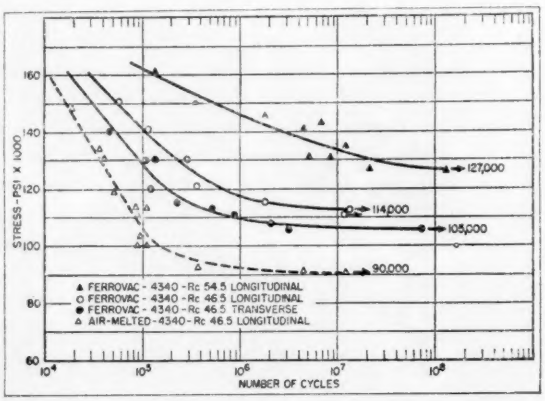

Table III (Below). Impact strength of FERROVAC 4340.

Tempering Treatment	*Hardness Rockwell C*	*Impact Energy Ft.-Lbs*
As quenched	57.5	15
300°F—2 Hours	56	22
400°F—2 Hours	53	21.5
500°F—2 Hours	50.5	17
600°F—2 Hours	49	17
700°F—2 Hours	47.5	18.5
800°F—2 Hours	45.5	24.5

ally isotropic with respect to endurance limit. Fig. 11 compares the endurance limit and ultimate tensile strength for vacuum melted and air melted SAE 4340.

A marked improvement has been noticed in impact properties of iron-chromium alloys after vacuum melting[12].

Forgeable alloys containing up to 49% chromium have been produced successfully. Vacuum melting resulted in either higher impact energy, lower transition temperature, or both, in all of the compositions evaluated. A comparison of the properties of 17% CrFe alloy and Type 430 stainless steel is shown in Fig. 12.

In spite of the demonstrable advantages of vacuum induction melting, such as those cited above, this process is not a 'cure-all' and, in some instances, the application does not justify the additional cost. Probably the most serious limitation at present is ingot size. The use of vacuum has little or no effect upon ingot solidification characteristics, and vacuum induction melting faces the same problems in this respect as air melting. The largest ingots now produced are approximately 15 inch. square. These do not permit the manufacture of extremely large billets desired for some applications and larger furnaces are required.

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CONSUMABLE ELECTRODE MELTING

This type of melting equipment has recently been utilised for the production of some high-temperature alloys and steels[13]. The apparent advantages of this technique are:—

(*1*) Ability to produce large ingots with sound centres,
(*2*) Relatively large melting capacity,
(*3*) Comparatively low melting cost, and
(*4*) Breakdown and redistribution of large non-metallic inclusions.

Experience in the titanium industry indicated that consumable-electrode furnaces—frequently called cold mould furnaces—representing a large potential melting capacity, could be built rapidly. As a result of the insistent demand for additional vacuum melting capacity, the advantages of this process have been studied and a great deal of work is now under way to develop markets for the material.

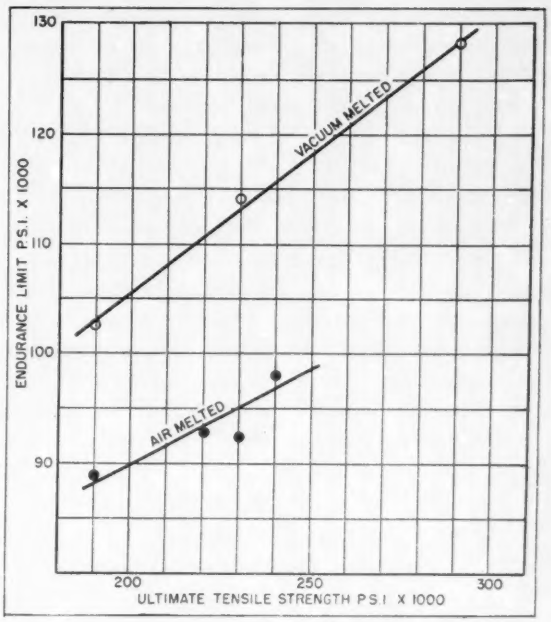
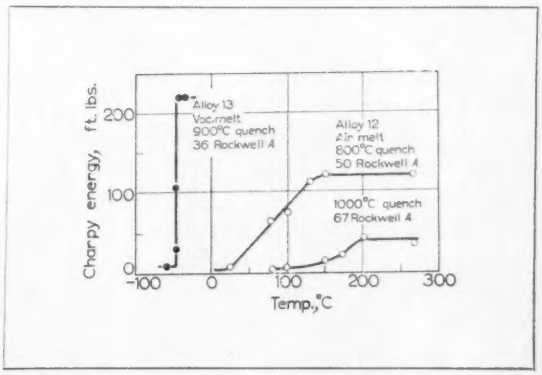


Fig. 11. A comparison of endurance limit and ultimate tensile strength for vacuum-melted and air-melted SAE 4340.

The most striking advantage of the process appears to be the ability to produce large diameter

Fig. 12. Charpy transition curves for vacuum-melted 17% Cr alloy and air-melted type 430 stainless steel.



ingots essentially free of centre porosity or segregation. Furnaces have been built that will be capable of producing ingots up to 30 inch. in diameter, weighing over 10,000 pounds each.

The quality of the resultant product is greatly dependent upon the starting electrode which is normally of air melted material. Both wrought and cast electrodes have been used and the choice for any particular grade will depend upon manufacturing costs. It is generally acknowledged that for most alloys purification during re-melting is limited and that the major improvement noted is the reduction in dissolved gases and the tendency to disperse large inclusions into a myriad of smaller and less objectionable ones. Metallographic examination of this type of material usually shows a general background of finely dispersed inclusions that are not considered objectionable for many applications.

High-vapour pressure materials, such as manganese, are vaporised from the tip of the electrode and the surface of the bath and recondensed on the mould walls. As the melt level rises in the crucible, these materials are re-melted and form an alloy-rich layer on the ingot surface. In many instances this results in a porous surface layer $\frac{1}{8}$-inch to $\frac{1}{4}$-inch thick that must be removed before the ingot is hot-worked. Since ingot soundness and surface condition are direct results of the melting rate, the operator cannot vary this at will. The only means by which he can control vaporisation losses is through the use of a partial pressure of an inert gas, such as argon. The variation in rates of vaporisation of different elements creates a chemical control problem in those alloys, having narrow composition ranges. Carbon is lost through reaction with residual oxygen in the electrode and this represents a serious problem in the case of many steel grades which have a carbon range of only 0.04% or 0.05%. Since the operator can do little to control the final composition of the ingot, it is necessary to produce an electrode to a metallurgical specification that will yield an ingot of the proper composition after varying amounts of different elements have been vaporised. This specification may in some cases be outside the normal air melting specification of the alloy and will require the production of special heats for use as electrodes.

Although this is not an insurmountable problem, it will in some cases result in high cost for electrodes which may offset the subsequent savings for the re-melting operation.

One alloy that appears ideally suited to production in cold mould furnaces is A-286. The specification for this alloy is:—

carbon	0.08 % max.
manganese	1.0-2.0 %
silicon	0.40-1.00%
lead	0.040 % max.
sulphur	0.020 % max.
aluminium	0.35 % max.
chromium	13.5-16.0 %
nickel	24.0-27.0 %
molybdenum	1.0-1.5 %
titanium	1.75-2.25%
vanadium	0.10-0.50%

It will be noted that carbon is low and that there are no narrow composition ranges for any element. Although this alloy is difficult to produce economically by air melting techniques, electrodes can be manufactured satisfactorily. A large tonnage of satisfactory material has already been produced by this process.

Vacuum induction melted material has properties equal to or better than those of the cold mould material and exhibits improved ductility. However, the product of the cold mould furnace consistently meets the specification at low cost and appears to be well suited for this application.

Evaluation of bearing steels and high-temperature alloys made by this process is now under way. A great deal of difficulty has been experienced in producing the titanium and aluminium bearing precipitation type (nickel based) high-temperature alloys largely because of the difficulty of producing a satisfactory electrode. For some applications requiring this type of alloy in large sections, it appears possible to produce the material by making electrodes in the vacuum induction furnace and subsequently re-melting them in a cold mould furnace.

The application of consumable-electrode melting furnaces to the production of steels and high temperature alloys is quite recent and a great deal of

additional development work will be required before the merits of the process can be fully evaluated. It holds a great deal of promise and appears to be one more tool for producing special-quality materials. It does, however, have severe limitations of its own that may prevent its use for some applications.

Equipment

Cold mould furnaces are of relatively simple construction in comparison to vacuum induction furnaces (Fig. 13). The electrode and crucible or 'cold mould' are enclosed in a vacuum-tight chamber and the only movement that must be controlled is the raising and lowering of the electrode with respect to the molten pool.

In most furnaces power is supplied to the electrode through a 'stinger rod' that is fastened to the top of the electrode and slides through a vacuum seal. This rod is also used as a part of the electrode drive mechanism to control the feed rate. A second design supplies power to the electrode housing itself and transmits the power to the electrode through sliding contacts. A third variation supplies power to the electrode by means of flexible leads inside the electrode housing. In the second and third type of furnace the electrode drive mechanism is also enclosed in the vacuum chamber, with motive power supplied from an external motor through a rotary shaft seal. This design tends to reduce the overall height of the furnace, but has the disadvantage of including more mechanical equipment inside the vacuum chamber.

In order to maintain stable arcing, close control over arc voltage is required. In many installations the operator simply adjusts feed rates manually to maintain the required voltage, while, in others, completely automatic controls are used. The possible explosion hazard in this type of furnace has resulted in a general practice of installing the furnaces in pits or behind blast barriers and performing all control functions remotely. Television cameras and optical viewers have been used extensively, while some operators rely entirely upon meter readings without any visual observation of the melting process.

High-amperage low-voltage d.c. current is supplied from a series of d.c. welding generators or selenium rectifiers. The more recent silicon rectifiers show promise and may soon be used widely. Arc voltages are commonly in the range of 20-35 V with an arc length of $\frac{1}{2}$ inch to $1\frac{1}{2}$ inch., while the current consumption is of the order of 800-1,500 A per inch of ingot diameter.

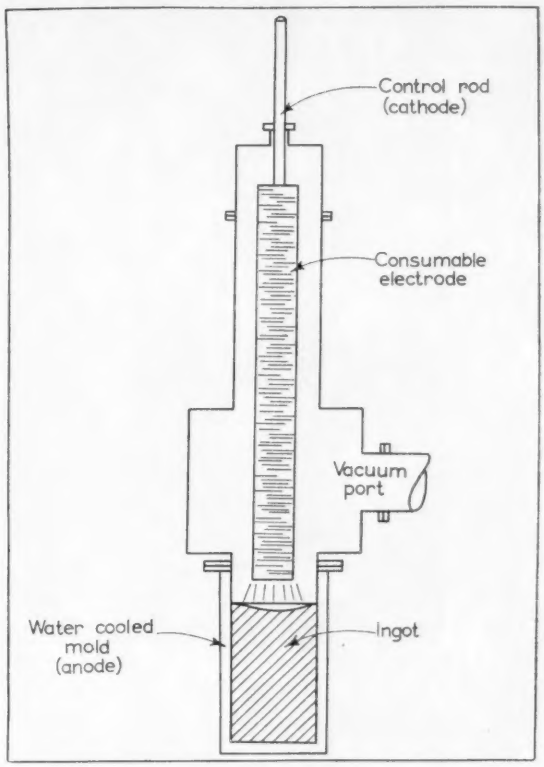
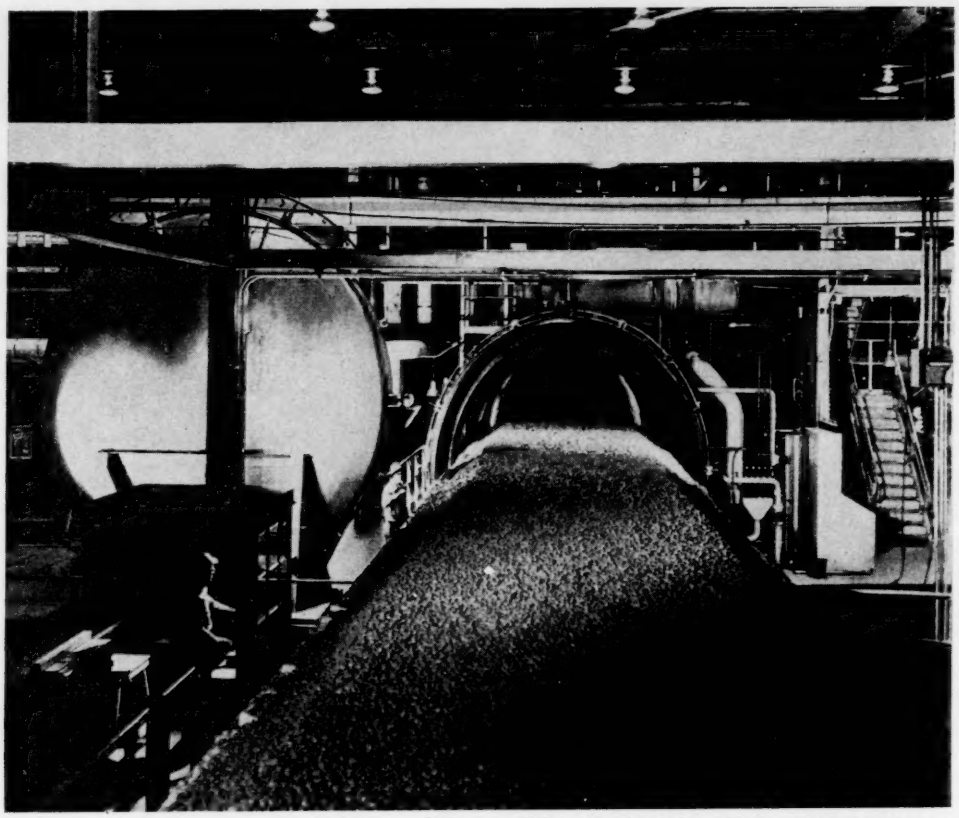


Fig. 13. Consumable-electrode vacuum arc furnace.

Although titanium has been successfully produced in furnaces operating in the millimetre range of pressures, recent work has demonstrated some advantages of operating in the low micron range[14]. Most of the consumable electrode melting of steels and high-temperature alloys has been in the low micron range of pressures and pumping equipment is similar to that used for vacuum induction melting.



by Courtesy of Electro-Metallurgical Co., Division of Union Carbide Corp.

Fig. 14. Loading vacuum furnace with raw pellets.

Studies of arc behaviour at varying pressures[15] have shown that there are advantages in operating at pressures in the low micron range. The arc itself tends to be more diffuse and the hazard of burning through the wall of the crucible is reduced significantly. The low pressures also hasten the removal of dissolved gases.

'SIMPLEX' LOW CARBON FERROCHROME PRODUCTION

One example of a truly large-scale metallurgical operation utilising vacuum technology is the process for producing 'Simplex' low carbon ferrochrome* (Fig. 14). This process, patented in 1949† removes the carbon present in high carbon ferrochrome to yield low carbon ferrochrome, based on the reaction:

$$2C + SiO_2 \quad 2CO + Si$$

High carbon ferrochrome and silica are ground to a very fine particle size, intimately mixed and compacted into pellets or other shapes. The compacts are then fed into the vacuum furnace and heated to

* The Electro-Metallurgical Co., Marietta, Ohio.
† U.S. Pat. No.2,473,019, Hendrik & de W. Erasmus.

1,150-1,400°C at which time the carbon and sulphur, if present, are pumped off as CO and SiS. In a typical batch, carbon is reduced from 4.5/5.5% to 0.025% maximum, and for some grades ot 0.01% maximum. Sulphur is reduced from approximately 0.07% to 0.02% maximum.

The unit used for this operation is the largest vacuum furnace in the world. It consists of a refractory-lined chamber approximately 17 ft. in diameter by 150 ft. long. The pumping system consists of a series of five-stage steam ejectors which are capable of evacuating the system to pressures of approximately 50 to 100 micron Hg.

This operation is an excellent example of the fact that large-scale vacuum equipment is feasible and, in some instances, provides the most economical method of processing.[16]

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SINTERING OF MIXED CARBIDES

The production of tungsten carbide shapes, either by hot pressing or the cold press and sinter process, utilising hydrogen sintering furnaces, is well established. Although both processes produce excellent material and each has advantages, it was recognised that for many applications a further improvement in properties was required and that this improvement could be attained by the addition of titanium carbide. Unfortunately, the reactive nature of titanium prevented the use of either process, and it became apparent that a vacuum sintering operation was required. The use of vacuum sintering equipment has proved to be quite practical and several manufacturers are in full production. Although nearly all hydrogen sintering furnaces are continuous three-zone units, most vacuum furnaces are batch-type units at present. Operating costs are low and in some cases they have been reported to be competitive with hydrogen furnaces. It appears probable that continuous furnaces will be placed in operation shortly and that additional cost reductions will result.

STREAM DEGASSING OF STEEL

The Bochumer Verein steel degassing process[17], developed in Europe, is also receiving a great deal of attention in the United States. Many steel companies have installed small-scale units for evaluation purposes, and there is at least one installation comparable in size to the large European plants.

Operation of existing facilities has been successful and further large-scale installations are planned. Vacuum systems for the large installations utilise five-stage ejectors. Hydrogen level in the ingots is reduced to approximately 50% of the normal value and flaking problems are virtually eliminated. A great deal of interest has been exhibited by people requiring large forgings, especially for high-speed rotating equipment, such as turbine and generator shafts. Although very little information has been published as yet, rapid expansion of facilities is anticipated.

CONCLUSIONS

An attempt has been made to provide a brief description of the current status of vacuum metallurgy in the United States. The examples cited are by no means complete, but are intended to indicate only that there is an increasing awareness of the fact that vacuum technology and equipment has arrived at a stage of development that permits the metallurgist to consider it seriously as a means of achieving improved metals and alloys for commercial applications. The merit of vacuum as a laboratory tool has long been recognised, but the recent developments in techniques and equipment have demonstrated that vacuum processing can be applied to large-scale metallurgical operations. In some instances it is a high-cost operation that produces superior materials not available by other methods of manufacture, while in other cases it is competing successfully even on a cost basis. The rate of expansion is extremely rapid and the diversification of application is increasing daily.

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VACUUM FUMIGATION

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Summary

SOME OF THE TECHNIQUES of fumigation employing reduced pressures are described. Recent investigations into the behaviour of the fumigant during treatments by these techniques and the effect of the technique upon the resistance of insects are reviewed. Features of some representative installations for vacuum fumigation are briefly described.

Sommaire

DESCRIPTION DE QUELQUES PROCÉDÉS de fumigation a pressions réduites. On passe en revue les recherches récentes faites sur le comportement du gaz pendant traitement par ces techniques et l'effet sur la résistance des insectes. Brève description d'installations pour la désinfection sous vide.

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INTRODUCTION

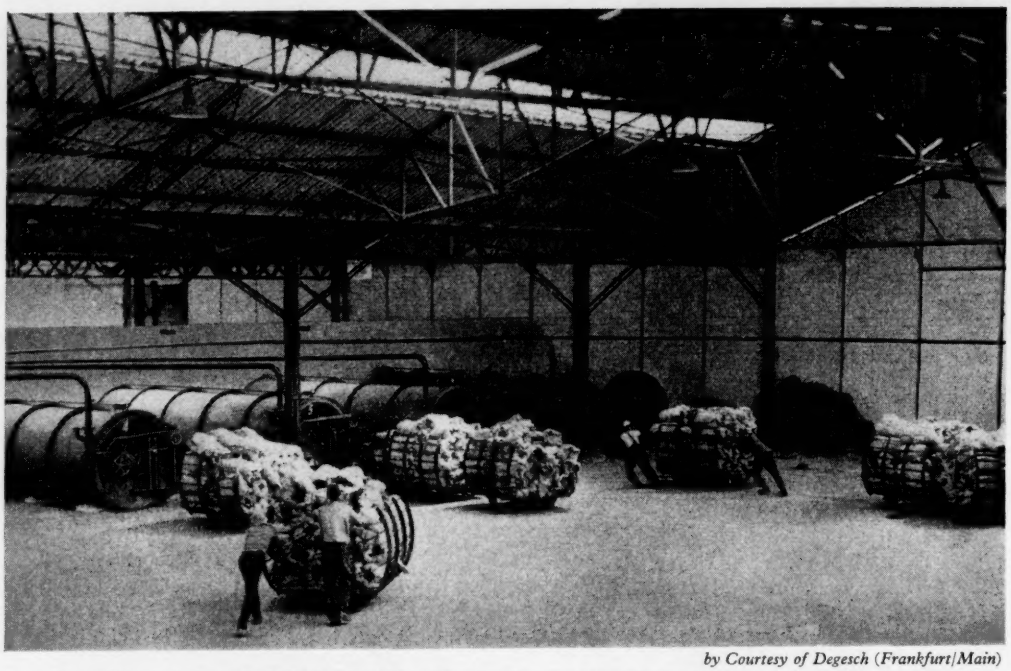
FUMIGATION PROVIDES a very important means for controlling infestation by insects and mites in a wide range of materials, for instance

> cereals and cereal products, pulses, oil seeds, animal feeding stuffs, cocoa, nuts and dried fruits; tobacco; natural fibres and clothing; hides and skins; timber and packaging materials; fresh fruits and growing plants.

A recent additional use of fumigation has been the cold sterilisation of such materials as hospital equipment and certain foodstuffs, for example, the spices used in the preparation of meat products. Fumigants have the ability to penetrate into packages and through bulks of material and to destroy the pests at all stages of their development, whether freely exposed or hidden inside granular material. To be effective, a sufficient concentration of the fumigant must be maintained for a sufficient length of time. It has been found that the toxic effect is usually related to the integrated product of concentration and exposure time. Any deleterious effect on the material is also usually related to the level of this 'c.t. product.' For this reason it is always desirable to employ a method of fumigation which will produce c.t. products throughout the treated material which are effective without being unnecessarily high.

A great deal of fumigation is carried out at atmospheric pressure in chambers, in sealed warehouses, in barges and ships' holds and under gas-proof sheets. In addition, many who undertake fumigation make use of special chambers, usually of steel, in which the pressure can be reduced substantially below atmospheric. The details of the technique are varied but all such methods are commonly described by the term 'vacuum fumigation.' In fumigation at atmospheric pressure, penetration of the gas to the centre of a bag or into a package may be quite slow and a relatively long period of treatment, say 24 hours or occasionally longer, may be necessary to ensure effective treatment throughout the material. Early tests showed that vacuum fumigation could be effective in much shorter periods, such as 1-4 hours. The time factor in itself is frequently unimportant, especially when dealing with a regular, large throughput of commodity, but

* M.S. received April, 1957

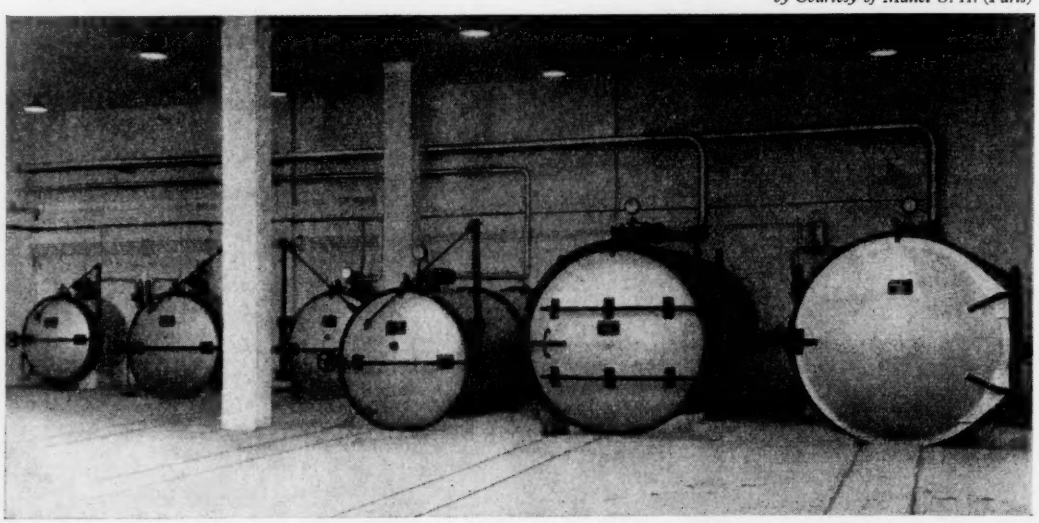


by Courtesy of Degesch (Frankfurt/Main)

Fig. 1 View of a large installation capable of fumigating 500 tons of mixed commodities daily. It comprises four chambers, each of 50 m.^{3} (1,750 ft.^{3}) capacity, and in addition one of 20 m.^{3} (700 ft.^{3}), one of 6 m.^{3} (210 ft.^{3}) and one of 2 m.^{3} (70 ft.^{3}). See also *Fig.* 7.

Fig. 2 View of a large installation comprising chambers of 70, 50, 20, 10, 4 and 2.5 m.^{3} (2,450, 1,750, 700, 350, 140 and 90 ft.^{3}) capacity.

by Courtesy of Mallet S. A. (Paris)



it is often claimed that the circumstances demand rapid treatment or at least make this a valued convenience. Thus, short period treatment in vacuum chambers is often adopted in quarantine stations where a wide range of products must be fumigated according to a variety of specifications.

Vacuum fumigation methods have a more obvious application in the treatment of those materials which are particularly difficult to fumigate at atmospheric pressure, such materials being leaf tobacco in bales or hogsheads, boxes of compressed dates and multiple packages of manufactured articles. It is further claimed for vacuum fumigation methods that they are intrinsically safer, since the treatment takes place in a vessel at reduced pressure from which no leakage can occur and residual gas remaining at the end of the treatment can be swept away before the chamber is opened. However, if similar engineering skill and care is given to the design and construction of chambers operating at atmospheric pressure these too can be made to operate with equivalent safety.

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EXISTING TECHNIQUES AND FUMIGANTS

Vacuum-Released Technique. Early workers on vacuum fumigation attributed the effectiveness of the short exposure periods permissible in that method to the ease with which the fumigant penetrated into packages once the obstacle presented by the intergranular air had been largely removed, and they thought this effect could be enhanced by restoring the pressure to atmospheric immediately after introduction of the fumigant. It was assumed that the inrushing air would drive the fumigant into the package. This method was referred to as the 'dissipated vacuum' or 'vacuum released' technique. There has been some criticism of these terms.[1]

Simultaneous Introduction of Air and Fumigant. In France and the French overseas territories a modification of this method was adopted which was widely used in vacuum fumigation installations there. This method resulted from rese_rches in Algiers[2,3] and is best described as 'vacuum fumigation with simultaneous introduction of air and fumigant.' After the initial reduction of pressure in the loaded chamber an air fumigant mixture is introduced of such composition that the desired dose of fumigant is delivered in full by the time the pressure has risen to a value a little below atmospheric.

Sustained-Vacuum Method. Other workers, for example in the United States and Canada, found that more effective treatment of the products they tested was obtained by maintaining the reduced pressure throughout the period of treatment. This method is usually referred to as the 'sustained-vacuum' method. It should be emphasized in this connection that the introduction of the dose of fumigant usually produces only a small rise in pressure. Means of stirring or circulating the air and fumigant within the chamber is sometimes provided.

Air-Washing Process. With all these techniques it has usually been customary, at the end of the period of treatment, to apply what has been termed an 'air-washing process.' In this, the pressure in the chamber is alternately reduced to a low figure and restored to atmospheric by the introduction of fresh air. It has been assumed that this process is particularly effective in removing the fumigant before the chamber is opened. In describing these various processes much confusion can be avoided if all low pressures are expressed in terms of absolute pressure and this practice will be followed here.

Fumigants. The above methods of vacuum fumigation were developed to allow more efficient use of the older fumigants such as hydrogen cyanide and ethylene oxide or mixtures of ethylene oxide and carbon dioxide. These fumigants have now been largely replaced by methyl bromide in the disinfestation of many types of stored products both at reduced pressures and at atmospheric pressure although the use of ethylene oxide for sterilisation against moulds and bacteria is increasing. Mixtures of acrylonitrile and carbon tetrachloride have been recommended for the vacuum fumigation of tobacco and tobacco products. Carbon disulphide is usually considered unsuitable for use in vacuum chambers because of its extreme inflammability, although at one time mixtures with carbon dioxide were in use.

RECENT RESEARCH ACTIVITIES AND FINDINGS

Fumigant Concentrations

A clearer understanding of the behaviour of the fumigant in these different processes has resulted from recent investigations, in which the variation of concentration of fumigant at selected points has been followed throughout the treatment by repeated gas-sampling and chemical analysis.[4–10] Tests made on a variety of commodities confirm that penetration of fumigant is most rapid with the sustained-vacuum method. Differences between fumigation at atmospheric pressure and the various reduced pressure procedures were more pronounced with the older fumigants, hydrogen cyanide and ethylene oxide.[7,8] Penetration of methyl bromide into coarsely granular products, such as wheat and groundnuts, was so rapid at atmospheric pressure that it was concluded[4,9] there could be little advantage in using vacuum methods unless there were some important biological effects associated with the use of reduced pressures. Important differences were obtained with this fumigant, however, in tests on products into which penetration is more difficult.[4–6,10]

Judged by the concentration measurements made during the fumigation period the results by the 'released vacuum' method and by the method with simultaneous admission of air and fumigant showed little difference from those obtained by fumigation at atmospheric pressure. In the sustained-vacuum method, however, much more rapid penetration to the centres of packages was obtained resulting in a more efficient distribution of fumigant in the short-period treatment. It was also found [4–6,10] that restoration of the pressure to atmospheric at a time when penetration had already taken place to a substantial degree, resulted in a sudden, large rise in concentration at the centre of the package. This is caused by contraction of the air-fumigant mixture which is within the package as the pressure rises. The phenomenon is not observed or is little pronounced and transient only, if the pressure is allowed to rise immediately after or during intro-introduction of the fumigant. It was suggested that this effect should be used to equalise the mean concentrations obtained at the surface and the centre of the package. However, all recent work has shown that the usual air-washing techniques are singularly ineffective in lowering the concentrations at the centre of a package of sorptive material and, as a result, the total integrated c.t. product for the fumigation and airing times together may be much higher at the centre than at the surface where the concentration rapidly falls to an ineffective level at the start of airing.

Further investigation is necessary to determine the best technique for any particular commodity. It has been suggested[6] that for some commodities excessive c.t. products at the centres of packages could be avoided by removal of the residual adsorbed fumigant at reduced pressure. This could be effected by continuous evacuation of the chamber while allowing a controlled admission of air to sweep away the fumigant from the free space, the absolute pressure in the chamber being maintained at a few centimetres Hg. Alternatively, the production of high concentrations at the centre might be limited by restoring the pressure to atmospheric earlier in the process or by a careful choice of the working pressure. Although the normal repeated air-washings have only a limited effect on the concentrations at the centres of packages the final restoration of the pressure to atmospheric has the effect of driving fumigant from the free space and surface layers of the package towards its centre, thus making it safer for persons to enter the chamber for unloading.[10] The evidence would suggest, however, that little is to be gained by employing more than one reduction of pressure during this airing process.

The efficiency of penetration in the sustained vacuum method is satisfactorily explained by the fact that the rate of diffusion of a gas through air is inversely proportional to the total absolute pressure. Thus, diffusion at a pressure of 7.6 cm. Hg is ten times as fast as at 76 cm. Hg and there is little, if any, effect on this ratio when the diffusion is occurring through the intergranular spaces of a mass of finely divided sorptive material, although the actual rates of diffusion will then be greatly

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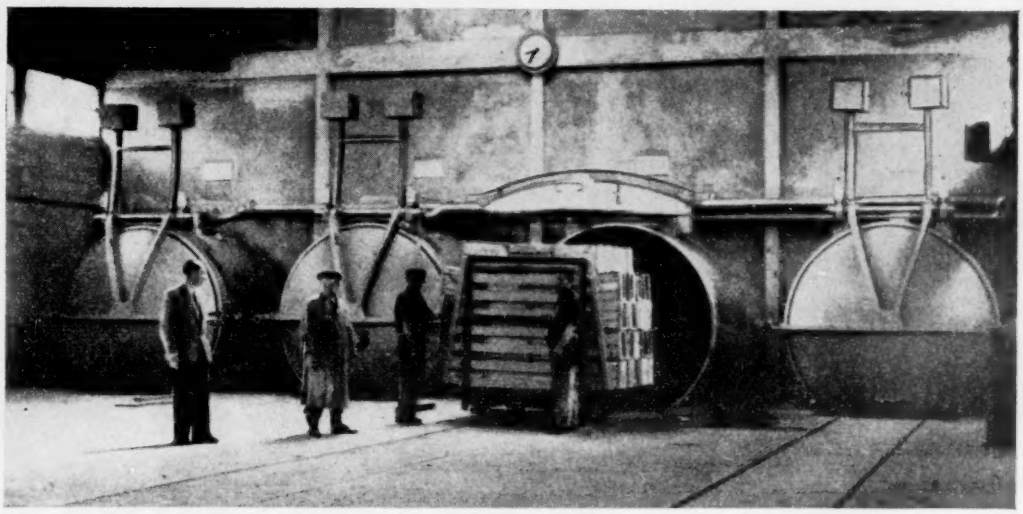
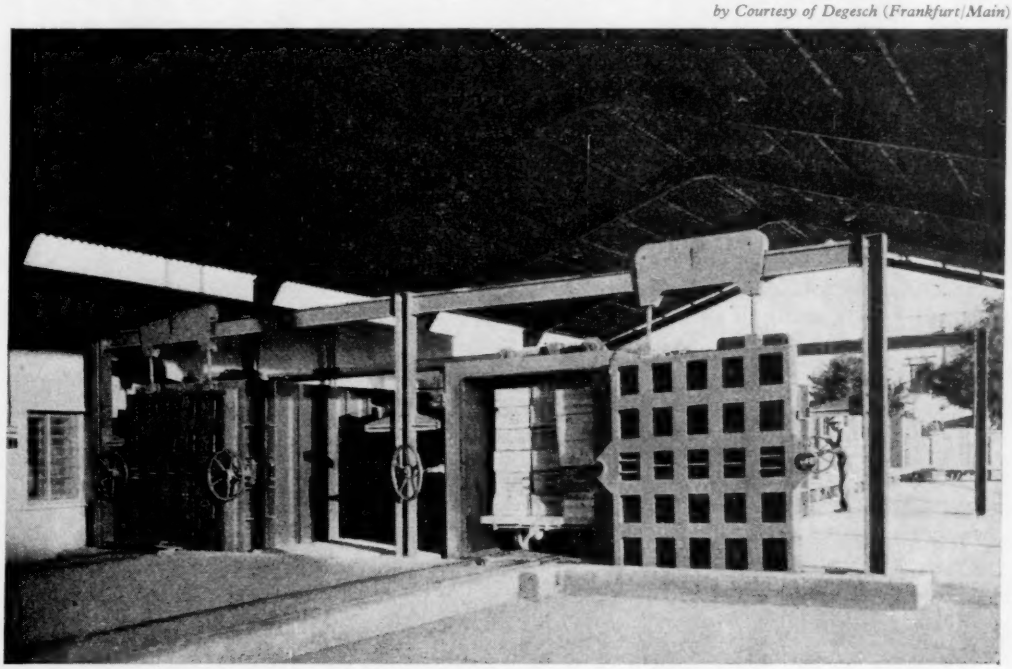


by Courtesy of Mallet S. A. (Paris)

Fig. 3 Cylindrical chambers with counterbalanced doors.

Fig. 4 Rectangular chambers of 25 m.^{3} (875 ft.^{3}) capacity used for the fumigation of boxes of dates.

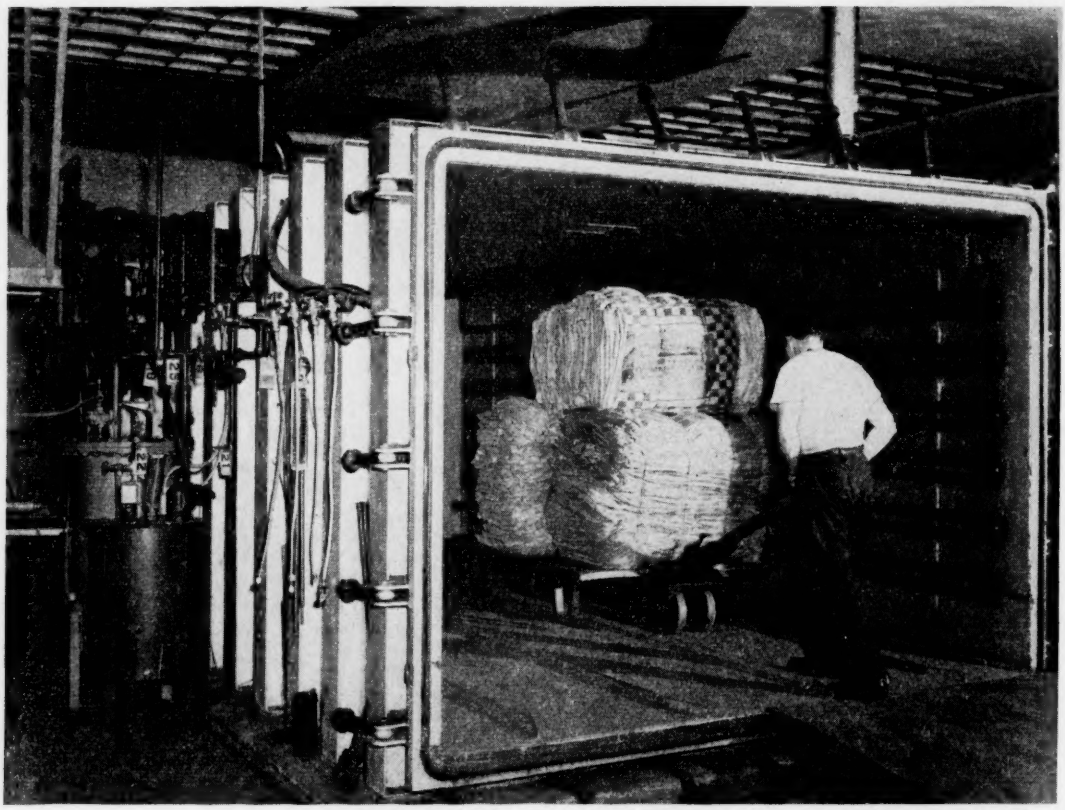
by Courtesy of Degesch (Frankfurt/Main)



reduced[5]. Sorption of a fumigant by a finely divided product freely exposed (*e.g.* in a thin layer) appears to be unaffected by the total pressure.[11] Sorption by freely exposed granular materials such as grains or pulses might be expected to be greater at lower pressures because of more rapid diffusion into the individual grains, but experimental data on wheat do not show this.[12]

Exposure to low pressure alone, in the ranges of pressure and time normally employed in vacuum fumigation, may produce a significant mortality with some insects but with others, such as adult grain weevils, there is little obvious effect.[13]

In recent investigations with methyl bromide[14,15] an attempt has been made to find out the extent to which the c.t. products required for a complete kill



by Courtesy of Science Service, Canada Dept. of Agriculture and the Editor of J. Sci. Fd. Agric.

Fig. 5 Rectangular chamber of about 35 m.^{3} (1,200 ft.^{3}) capacity operated by the Canadian Government.

Insect Mortality

The effects of variation of pressure upon the response of insects to particular concentrations of fumigants have frequently been offered as an explanation of the effectiveness of vacuum fumigation methods.

in fumigations at reduced pressure differ from those required at atmospheric pressure. These tests were made on insects exposed in an empty chamber. Factors which affect the comparison are the species and stage of insect, the temperature, the relative humidity, the absolute pressure and the period of

reduced pressure. In most cases the insects were more susceptible at reduced pressure than at atmospheric pressure, sometimes by a factor of between 2 and 3, but in other cases there was little or no difference. Thus in tests on all stages of the grain weevil in wheat grains, although the order of resistance of these stages differed in the different fumigation techniques, it was concluded that the c.t. product required for a high percentage kill (99.9) of all stages was little affected by the technique.

There is some evidence,[12] clearest in tests on adult grain weevils with hydrogen cyanide, that the shape of the concentration-time curve affects the response of the insects to a particular c.t. product, and that the optimum effect is obtained when the concentration rises rapidly at the start of the fumigation. This effect would contribute to the efficiency of the sustained vacuum method in which penetration to the centres of packages is more rapid than in other methods.

On the whole it would appear that it will seldom be possible to rely upon a marked increase in susceptibility to the fumigant resulting from the use of a particular technique of vacuum fumigation. Although this effect may sometimes be of considerable practical importance, it will usually be necessary to base the selection of fumigation technique first of all upon the achievement of an even distribution of c.t. products throughout the treated commodity within the fumigation and airing periods.

The minimising of the time taken for a complete cycle of operations will usually be the second most important consideration, and, in practice, some compromise between these needs may have to be accepted.

Assuming that the technique achieves an even distribution of c.t. products, then the shorter the fumigation time allowed, the larger the dose of fumigant which will be required. In general, the doses of fumigant required in vacuum fumigation, with the relatively short periods of fumigation which are customary, are greater than in fumigation at atmospheric pressure over the usual periods of 24 or 48 hours, though according to much of the older published evidence, the differences are less than might be expected.

ENGINEERING OF VACUUM FUMIGATION PLANT

Full advantage can be taken of the greater speed of fumigation possible in a vacuum chamber only if the installation allows rapid loading and unloading of goods and efficient control of all operations. In many of the larger, commercial installations the goods are loaded on to low trolleys or trucks which can be quickly pushed into, or out of the chamber, see Figs. 1-4. Where the trucks run on rails, moveable sections of rail must be provided for bridging the gaps at the chamber doors. Alternatively, the goods can be handled on trays or pallets, see Fig. 5. Vacuum fumigation chambers are frequently housed in a building which has been specially designed as a disinfestation or quarantine station, complete with control and machinery rooms, laboratory and offices. Fig. 6 shows the layout for a small station containing one large and one small chamber. These have doors at both ends and are erected through a wall which divides the main hall into a 'dirty' side where the infested goods are received and loaded into the chambers, and a 'clean' side where the fumigated goods are taken from the chambers and despatched. This segregation of infested from fumigated goods is most desirable and, particularly where flying insects may be encountered, the dividing wall should be extended to the roof to provide a complete insect barrier. The layout in Fig. 6 provides for delivery and collection of goods by road, and for fumigation on trolleys running on a rail system.

The fumigation controls are grouped in a control room adjacent to the rooms housing pumps and other equipment. Figs. 7 and 8 show parts of the control rooms in two large installations with recording instruments and various visual aids to correct operation. A variety of automatic devices can be incorporated into the installation to prevent faulty operation or damage to the pumps, and to safeguard the operators.

Of course, the smaller types of vacuum fumigation plant such as might be required in a factory for occasional treatment of either raw materials or

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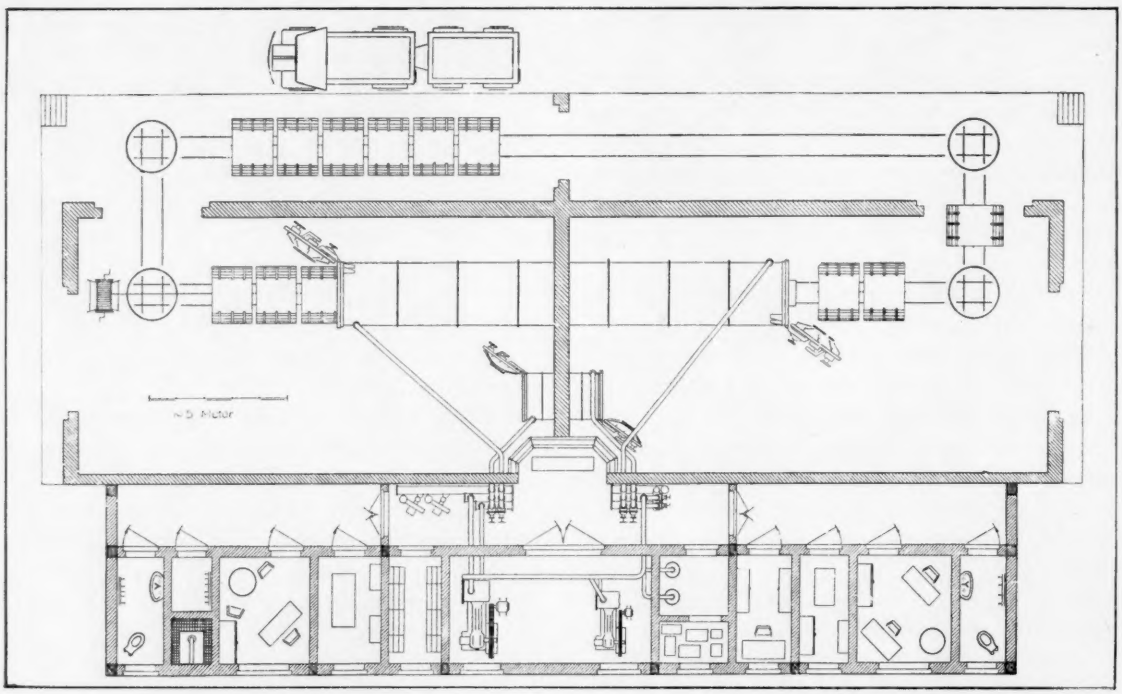
finished products, can be compactly arranged in a relatively small space, see Fig. 9. Small vacuum fumigation units have sometimes been mounted on a lorry (Fig. 10) or trailer.

Chamber Design

Chambers are almost invariably of welded steel construction. A cylindrical chamber is cheaper to construct than a rectangular chamber of equal capacity, but the latter is sometimes preferred for

dished either inwards (Fig. 1) or outwards (Figs. 2 and 3) but in rectangular chambers a flat door is usually designed with suitable reinforcement—(Figs. 4 and 9). The door may be hinged at the side (Figs. 1, 2, 9 and 10), or it may be hinged at the top and counterbalanced (Fig. 3).

Alternatively, it may slide to the side (Fig. 4), or swing to the side by means of a davit (Fig. 5), or lift upwards (Fig. 11). Where hinges are used they usually allow some freedom of movement so that



by Courtesy of Degesch (Frankfurt/Main)

Fig. 6 Design for a disinfestation station comprising one chamber of 50 m.^{3} (1,750 ft.^{3}) and one chamber of 5 m.^{3} (175 ft.^{3}) capacity, showing the loading and unloading facilities, a control room, rooms housing the vacuum pumps and other apparatus, offices and store rooms.

cased goods because of better utilisation of the space. The shell is usually reinforced by welding rings or girders on to it. Fig 11 shows an unusual chamber of reinforced concrete construction designed to take full-size railway wagons.

Doors may be provided at one or at both ends of the chamber. In cylindrical chambers they are usually

the door may be drawn tightly on all sides against a soft rubber gasket. In the chambers illustrated in Figs. 2, 3 and 10, a hollow tube is used as gasket, and the seal between chamber and door is effected by pumping air or water into this tube. Many doors are fitted with special mechanisms for rapid closing.

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Fig. 7 The control room for the installation illustrated in *Fig.* 1.

by Courtesy of Degesch (Frankfurt/ Main)

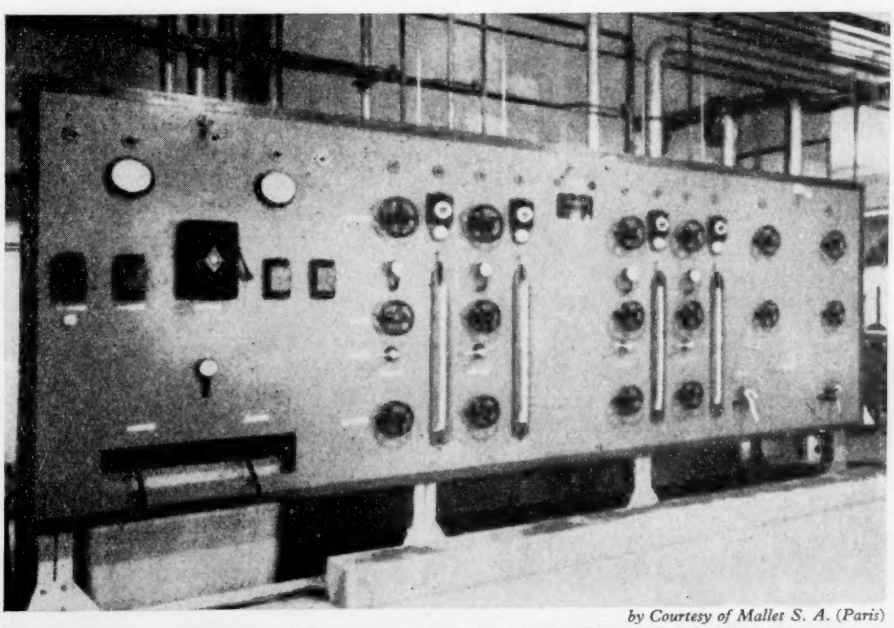
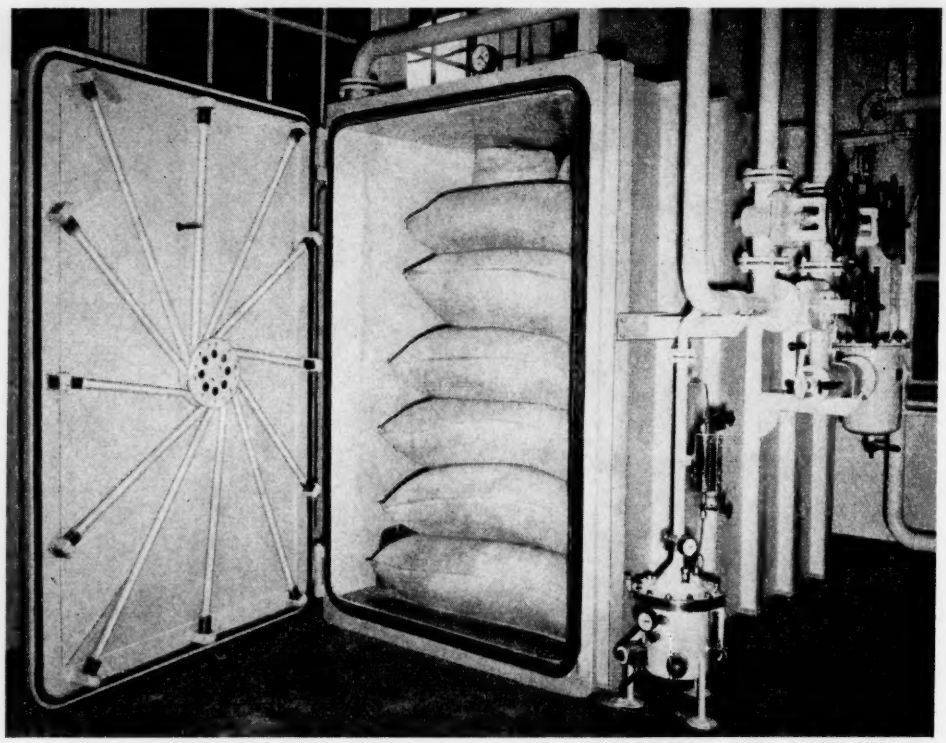


Fig. 8 The control panel of an installation consisting of four chambers.

by Courtesy of Mallet S. A. (Paris)

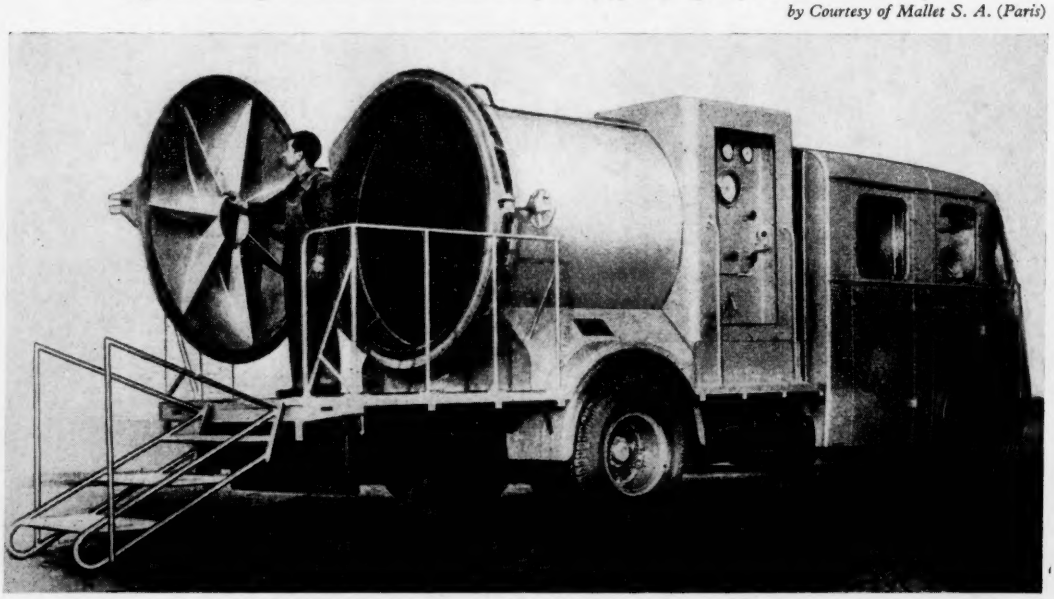


by Courtesy of Degesch (Frankfurt/Main)

Fig. 9 A compact installation with a chamber of 5 m.^{3} (175 ft.^{3}) capacity.

Fig. 10 A fumigation unit with a chamber of 5 m.^{3} (175 ft.^{3}) capacity mounted on a lorry.

by Courtesy of Mallet S. A. (Paris)



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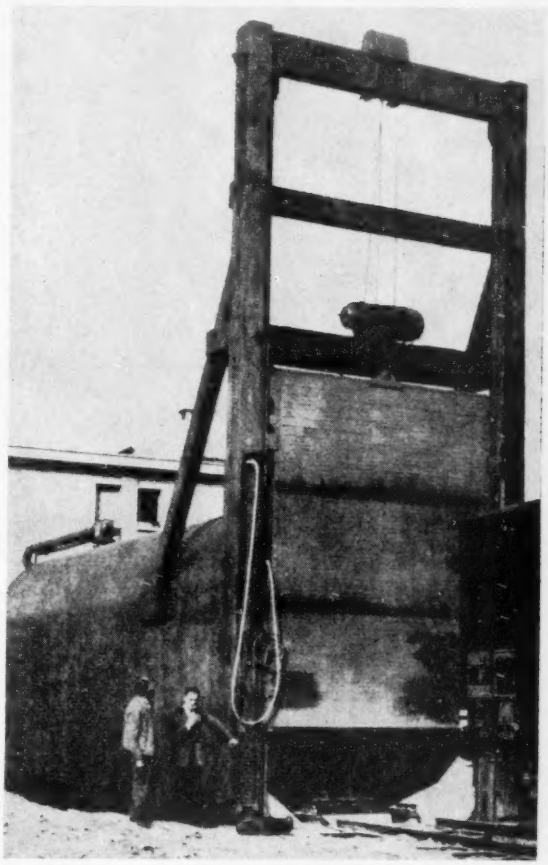
Pumps and Pumping

The pumps may be of a rotary or a reciprocating type. The plants illustrated in Figs. 2 and 3 employ rotary vacuum pumps whereas the plants shown in Figs. 1 and 4 are provided with large single-stage, slow-speed piston pumps. The performance is usually such that the pressure in the chamber can be reduced from atmospheric to the normal working level in less than ten minutes. Views differ as to the amount of pressure reduction required in practice. In some plants the pressure normally employed is around 12.5 cm. Hg absolute. More frequently a pressure of about 5 cm. Hg is used and some workers vary the reduced pressure according to the type of commodity treated. Pressures as low as 1 cm. Hg have been suggested for some finely divided products[17].

Circulation. In some plants, operating on the sustained-vacuum technique, pipe connections are arranged so that after the initial evacuation the pump can be used to circulate the residual air through the chamber during the introduction of the fumigant and for a period of 5 to 15 minutes afterwards. It has been stated[18] that the increase in efficiency of distribution of fumigant resulting from this circulation permits a useful reduction in dose.

When this type of circulation is not employed it has been found advantageous to introduce the vaporised fumigant at multiple gas-inlets arranged, for example, along the four longitudinal angles of a rectangular chamber. In a small chamber use of a stirring fan, mounted on a shaft passing through a vacuum-tight bearing, is sufficient to ensure even distribution of fumigant through the free space of the chamber.

Fumigant Introduction. The apparatus provided for the introduction of fumigant varies according to the choice of fumigant and the method of vacuum fumigation employed. For liquid fumigants such as methyl bromide, ethylene oxide or hydrogen cyanide a heated vaporiser with water or steam jacket is usually provided. In some German plants where the system of circulating at reduced pressure is employed, the pressure at the outlet side of the pump is adjusted by means of a regulating valve to about one atmosphere. The heat produced at this point can be utilised for vaporisation of fumigant. Thus, when the absorbed form of hydrogen cyanide fumigant is used, this warm air stream is passed through the generator which incorporates a can-opening device and it is claimed that vaporisation is complete within a few minutes.



by Courtesy of Mallet S. A. (Paris)

Fig. 11 A large chamber of reinforced concrete construction designed to take railway wagons.

Where the method of vacuum fumigation with simultaneous introduction of air and fumigant is employed, a counter-balanced gas holder is provided to hold the vaporised fumigant at atmospheric pressure. From this it is withdrawn and mixed in the correct proportion with air in a special valve at the entry to the chamber.

The dose of liquid fumigant is measured by weight during delivery from the cylinder or by application through a calibrated glass vessel.

Ventilation and Heating

In most installations the vacuum pump is used to remove fumigant remaining in the chamber at the end of the treatment. Usually the pressure is alternately reduced to a low figure, about 5-10 cm. Hg and restored to atmospheric by the introduction of fresh air as described earlier in this paper. In some of the larger German plants, however, after raising the pressure to atmospheric, the fumigant is swept out at this pressure by a high pressure blower, and repeated reductions of pressure are given only in cases where it is thought that efficient removal of gas is particularly important or difficult.

Many chambers in the colder countries are provided with some means of heating. This should assist satisfactory distribution of the fumigant. Any rise in temperature is also likely to increase the susceptibility of the insects present, but, of course, many types of package would have to remain in the chamber for a considerable time before such heating could affect the inner layers. It may be more practical to arrange for the commodity to be brought to a suitable temperature before it is loaded into the chamber.

CONCLUSIONS

Although vacuum fumigation methods have been in use for more than forty years and considerable engineering skill has been applied to the design of such installations, there is still a confusing variety of views on the respective merits of the different operating procedures. Recent investigations have shown how variations of technique can effect the behaviour of the fumigant and the expected efficiency of the treatment. In many respects the picture is more complex than was visualised by earlier workers, and further experimental work will be required to establish clearly which techniques are best suited to the treatment of particular commodities.

The basic requirements for a vacuum fumigation plant are, however, likely to remain, as now: One or more chambers of a design which allows rapid loading and unloading and closure of the doors; vacuum pumps for reducing the pressure of a chamber to 2-3 cm. Hg within 10 minutes; means for measuring and vaporising the dose of fumigant, and instruments for indicating or recording pressures in the chambers. It is advantageous, in the case of larger chambers, to provide means for stirring or circulating the air and fumigant in the chamber during, and for a period after, the introduction of the fumigant, and in temperate climates some heating of the chamber is probably worthwhile.

Vacuum fumigation methods are most worthy of consideration in stations undertaking disinfestation of a wide variety of commodities for the purposes of quarantine or in connection with processing plants where rapidity of treatment is considered to be of paramount importance. Vacuum fumigation is unlikely to compete economically with fumigation at atmospheric pressure for the treatment of very large bulks of commodity, particularly of those stored in circumstances which allow fumigation without any additional handling.

This paper is published by permission of the Department of Scientific and Industrial Research. Grateful acknowledgment is made to Deutsche. Gesellschaft für Schädlingsbekämpfung m.b.H, (Degesch), Frankfurt (Main), to Mallet S.A., Paris and to the Canadian Department of Agriculture, Science Service, for permission to publish the various pictures accompanying this article. All these organisations have also been kind enough to provide information on the design and operation of vacuum fumigation installations. Certain features of some of the plant referred to are subject to Patent regulations.

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EARL W. FLOSDORF

1904
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The news of the death of Dr. Flosdorf early this year reached us a few months after we had received his manuscript for the article on the opposite page, and only a few weeks after we had made his personal acquaintance, while on his last trip to Europe. Thus, the impact of this tragedy on us was the more severe as our impressions of his amiable and attractive personality were still fresh. Unquestionably, Dr. Flosdorf was as great a friend of humanity as he was a scholar and scientist.

Dr. Flosdorf was born at Philadelphia in 1904. He graduated at Wesleyan University, Middletown, Conn., and was awarded his doctorate at Princeton. He began his professional career as a lecturer of chemistry. This was followed by research work in medicine facilitated by a grant and leading to the appointment of Assistant Professor of Bacteriology at Pennsylvania University. This post he held for ten years and it was during that period that he became first interested in freeze drying. His work on the development of methods and equipment for the preparation of blood plasma and sera by that technique eventually laid the foundation for the general U.S. Red Cross (Army-Navy) blood programme, put into operation at the outset of World War II.

In early 1941, Dr. Flosdorf was appointed Director of Research at F. J. Stokes Corporation, a position he still occupied at the time of his death. He retained his interest in freeze drying, improving the method and extending its application to new fields such as the processing of food.

Dr. Flosdorf has published some eighty articles currently reporting on the results of his work. His book, *Freeze-Drying* (*Drying by Sublimation*), published in 1949, was the first solely devoted to this subject. In addition, he was granted forty-five patents.

Dr. Flosdorf's contribution to the progress of science and technology received full recognition during his lifetime. He was a member of fifteen scientific societies and was appointed an Honorary Member of the Walter Reed Society.

The *avant-garde* of vacuum scientists and technologists, to which Dr. Flosdorf belonged, is still small in number and his exceptional gift of co-ordinating scientific and engineering problems will be missed by all who work for the promotion of the art, particularly, in the field of freeze drying.

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Vacuum, Vol. VI

VACUUM DRYING

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Samuel C. Tease

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Research and Development Division,
F. J. Stokes Corporation,
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Summary

A DETAILED SURVEY is made of the present state of the art of vacuum drying with particular reference to freeze drying. The author proceeds to discuss the various forms of pumping plant employed in the technique as well as the different types of drying equipment presently available on the market. A large part of the article deals with the physics of evaporation and engineering details of double-effect and similar evaporators employed in the concentration of fruit juices. Finally, the merits of vacuum or freeze drying various foods are studied.

Sommaire

UNE EXPERTISE DÉTAILLÉE est faite sur l'état actuel de l'art de séchage sous vide se rapportant en particulier à la technique de lyophilisation. L'auteur continue en discutant les divers modèles de pompes a vide employées dans cette technique, ainsi que les différents types d'installations de séchage actuellement en vente. Une grande partie de l'article traite de la physique de l'évaporation, des details de construction et performances des évaporateurs à double-effet, et des modèles semblables, employés dans la conçentration du jus de fruit. Finalement, les mérites du séchage sous vide ou de la lyophilisation de divers produits alimentaires sont étudiés.

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INTRODUCTION

Vacuum Drying—General

DRYING UNDER vacuum requires equipment more costly than that for atmospheric drying. This is because of the obvious strength characteristics needed to withstand the external atmospheric pressure of 15 psi. Because of this, there must be major compensating advantages to justify vacuum-drying.

The major compensating advantage is the superiority of product which results from processing at lower temperature. The absence of oxygen under vacuum constitutes a further advantage with some materials because of oxygen sensitivity as well as heat sensitivity. The increased rate of drying under vacuum may, in some cases, also contribute.

In a word, the major reason justifying the use of vacuum in drying is to produce superior quality in the final product. Sometimes, in the extreme, it is the only method by which a product of acceptable quality can be obtained. In isolated instances, there may be other factors which enter into the use of vacuum and these will be referred to in the subsequent discussion.

Freezing and Freeze Drying

Indeed, in order to produce an acceptable product, it is necessary at times to go to a greater length and use higher vacua and lower temperatures so that the moisture may be sublimed from the product while frozen. This method, known as freeze drying, had its origin about 20 years ago, first as a laboratory-known process only. It subsequently was extended rapidly into industrial production. This happened

* MS. received August, 1957.

in large measure, as a result of institutional laboratory and industrial research in the fields of microbiology, serology, immunology, chemistry and pharmaceutics. Initially products manufactured commercially in this way were largely for human and veterinary medicine. More recently, however, extension into the production of foods has shown an active growth and attracted appreciable interest. Certain types of food and foods to be distributed under specialised conditions are more advantageously handled as freeze-dried products than as frozen products. This is true even in the United States and Canada, where the frozen food distribution system has grown to proportions so great that frozen products are available in the smallest and most remote hamlets. Frozen food includes everything from seafood products, such as whole fish, fillets, shellfish, (such as oysters and shrimps) to all ranges of vegetables and fruits, soups, juices, all meat and fowl products, and even complete meals arranged with individual servings as on so-called 'TV platters'. Frozen products have cut in severely on the sale of ordinary canned food, as well as fresh food. In spite of this condition, interest in freeze-dried products is expanding rapidly just now, as will be seen.

Additional Objectives which may be attained by the use of lower temperature and higher vacuum as applied in freeze-drying may include one or more of the following:

High Stability. In many cases a temperature below freezing-point is required to avoid chemical change in labile components during drying. This applies to blood plasma and serum, to most viruses, to many bacteria and other forms of micro-organisms, and to various other biological and pharmaceutical materials.

In addition to the preservation of micro-organisms such as viruses and bacteria for ordinary laboratory purposes, there is the major application to the distribution and storage of attenuated or modified strains. Examples are hog cholera, Brucella abortus, Rinderpest, BCG for tuberculosis and others used as vaccines in veterinary practice as well as human.

Low Volatility. Because of the low temperature, the loss of volatile constituents is small. Although the process takes place in vacuum with some attendant loss of volatile components into the vacuum system, such loss is usually very small. Toward the end of drying, when the products reach a higher temperature, virtually all the moisture has been removed, so that then there is practically no vapour distillation of volatiles. For example, the powder remaining after freeze drying fresh orange juice has little or no odour. Upon opening a sealed can of the dried juice and smelling it, one may be disappointed to find no odour comparable with that of fresh juice. However, upon reconstitution with water and aeration by shaking, an excellent aroma develops. The reconstituted mixture obtained is like fresh juice. This is a particularly important feature of the method in applications to many foods.

Exclusion of Foaming Phenomena. Because the product is usually frozen solid, there is no bubbling or foaming, even when dried well above the temperature at which there is eutectic separation. Changes due to surface action are thus avoided. This is particularly important with protein material. One of the best examples is the successful drying of blood plasma without loss in potency of any of its constituents.

Permanent Dispersion. In most cases, the solute remains evenly dispersed without undergoing concentration as the frozen solvent sublimes. As a result, the remaining dry residue emerges as a highly porous framework, occupying essentially the same overall space as the original solution. The final residue is not the fine powder with which the chemist is familiar; rather, it has a friable interlocking sponge-like structure. This is a major factor contributing to the extremely rapid and complete solubility of freeze-dried products.

Minimum Coagulation. Since the molecules of solute and colloidally dispersed particles are virtually 'locked' in position as the solvent evaporates, the tendency towards coagulation of even lyophobic sols is negligible. This is particularly important in the case of a great number of medicinal preparations.

Absence of Case-Hardening Effects. In drying from the frozen state, there can be no continual mixing of

solution or any other physical movement of solvent. The surface of the evaporating frozen ice layer gradually recedes and leaves more and more of the highly porous residue of dry solute exposed. As a result, 'case-hardening' never occurs. This accounts in part for the considerably lower amount of residual moisture in the final product which is obtained when the final temperatures employed in the process are not excessively high. Because of the lower moisture content, a greater degree of stability is imparted to thermo-labile materials than by any other method of drying.

Maximum Sterility. Bacterial growth and enzymatic changes cannot take place under the frozen conditions of drying. This is important for foods as well as for medical products used parenterally. Likewise, the final fully-dried product resists bacterial growth and enzymatic action. It is difficult in commercial production to be certain of complete asepsis at every stage of manufacture.

Speaking of injectables, particularly of those which, because of their nature, cannot be sterilised by filtration, by heat or chemically, there is always a possibility that just a few organisms may exist in the whole of the batch. As a result, it is possible that a few of the final ampoules are actually contaminated and, because of their number being low, these, during random selection testing might be missed. As long as the material is liquid, these few organisms have the chance to multiply undetected in the affected ampoules and while being stored the containers in question would become contaminated grossly. With a dry product, however, there is no opportunity for multiplication of organisms before the product is reconstituted for use. Since it then is employed immediately (and directions should always provide for this), there can be no harm to the recipient from the few organisms which may be present in occasional containers.

GENERAL PROCEDURES AND TYPES OF EQUIPMENT

Whatever the range of vacuum employed, a means of pumping the non-condensable gases must be provided. In addition, the evaporated water vapour must be removed. The latter may be accomplished either by condensing or by direct pumping. In the case of direct pumping, comparatively large pumps are required because the volume of the water vapour is much greater than that of the air to be removed. The vessels employed for holding the product from which the water is being removed during vacuum drying may assume a wide variety of forms. Selection for a given application depends upon many factors including the actual vacuum and temperature employed, the type of product processed and the capacity requirements. Either batch or continuous operation may be desirable.

The specific types of equipment which are used for these various functions will be presented in relation to the procedures applied, and to any modifications of the same. These will be illustrated with examples of commercial equipment and plant installations.

Sources of Vacuum

Non-Condensable Gases. Pumping of air and other non-condensable gases may be carried out by mechanical pumps or by means of steam ejectors.

Mechanical pumps are generally of two types, one reciprocating and the other rotary oil-sealed. The reciprocating pumps simply comprise an ordinary piston and valve arrangement similar to an air compressor. Indeed, by proper changing of piping connections, the same machine may be used for either purpose, thereby achieving lower manufacturing cost by using the same basic castings in greater production. These pumps are sometimes arranged in series to provide two-stage operation. For single-stage operation, a pressure of 27 to 28½ inch. Hg. reduced pressure represents about the limit of efficient operation. In two-stage operation, this may be extended to as high as 29½ inch. Hg. Water-sealed vane and turbine pumps are also used, but not to any great extent in drying at a really high vacuum. Oil-sealed rotary pumps find a wide application and, in single-stage operation, a blank-off

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pressure of around 1 μ Hg absolute pressure may be reached. In practice, however, a drying system built around such a pump will never reach a vacuum as high as that. A two-stage rotary pump on a comparable basis may reach a blank-off pressure as low as 0.01 μ Hg absolute pressure.

Rotary pumps frequently 'back-up' vapour pumps of the well-known oil ejector type and oil diffusion type. Both these utilise an integral boiler with return of the condensed vapour to the boiler. These may be operated as single-stage or multi-stage units. Likewise, oil vapour booster pumps with higher vapour velocity may be used to operate in an intermediate range between the diffusion and the rotary fore pump.

A typical peak pumping speed of oil booster pumps lies in the range of 1 to 20 μ Hg, blanking-off at pressures as low as 0.01 μ Hg with the high pressure pumping point lying as high as 1,000 μ Hg or even more. Fore-pump pressure in such a case may be as high as 1,000 μ Hg with the oil booster pump operating at 10 μ Hg.

The oil diffusion pump operates in more or less parallel fashion at lower pressures, but in drying procedures ordinarily it is unnecessary to go below the oil booster pump pressure range, even in freeze drying. In ordinary vacuum drying, above freezing, oil vapour pumps are not applicable.

Steam ejectors are widely used in drying operations and, according to the pressure requirements for the particular operation, with as many as five stages. High vacuum multi-stage ejectors are required only in freeze drying operations. The choice of steam ejectors or mechanical pumps depends on the relative cost of steam and cooling water for the ejectors, large quantities of both being needed, *versus* electrical power cost. Any saving shown must be balanced against the manufacturing

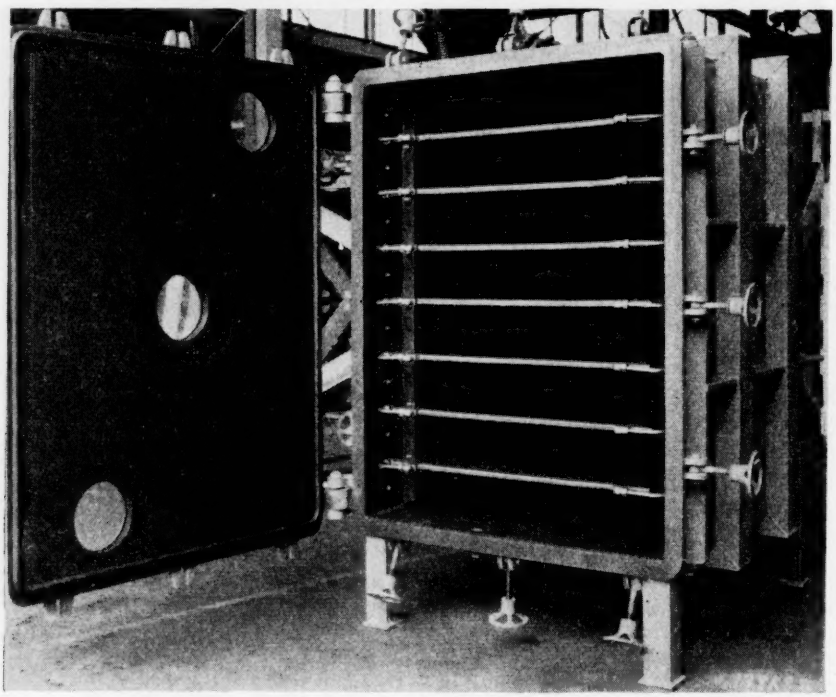

Fig. 1. Shelf dryer.

cost of both the pumps and the steam ejectors. The manufacturing cost of the latter is generally lower than that of mechanical pumps if the cost of the steam boiler and its installation are neglected.

Water Vapour. In any drying operation the water vapour, as well as other condensables, must be removed. Strictly speaking, this is a pumping operation but condensers may serve the purpose by establishing low water vapour pressure. If the condensables are pumped directly any of the various types of pumping means described in the preceding section can be employed. However, the volume of the water as vapour is usually quite large in comparison with the non-condensable vapour to be pumped and accordingly the pumping capacity requirements are vastly increased. The same considerations apply in making the choice from all the various means available.

In the higher ranges of vacuum, for example in freeze drying, contamination with water of the sealing oil in the mechanical pumps must be avoided. There are several ways of accomplishing this, notably by heating the oil to drive out the water, separating it continuously by centrifugal action or by application of the well-known gas ballast principle. The latter is more limited with respect to capacity than other available means. However, today, condensation is usually the method of choice for removal of the water vapour in batch operations, rather than direct pumping, because of the lower cost of mechanical refrigeration units which are available for chilling the condensers. Continuous dryers introduce other considerations.

The area of surface available for the removal of water vapour, either in the form of liquid water or, in the case of freeze drying, as ice, is a critical factor. For condensation in the form of ice the surface may be cooled by direct expansion of suitable refrigerants, like ammonia, Freon, and others such as methyl chloride, but the last is outmoded in recent years in the United States of America and Canada.

The various Freons are most widely used, except for large tonnages in the temperature range down to approximately -30 to $-40°C$. In this range, ammonia has a definite part to play by arranging for compound operation. Under all other conditions Freons are the refrigerants of choice, both in the case of small capacity plant operating at any temperature and in the case of large capacity plant operating at temperatures below the ammonia range. Freon-12 is lowest in cost and, in single-stage operation, suitable for temperatures down to about $-40°C$. By compounding, considerably lower temperatures may be reached. However, at lower temperatures, Freon-22 is preferable, and finally at dry-ice temperatures or lower still, Freon-13, when employed in cascade combination with Freon-22, provides high efficiency. Methyl chloride and other refrigerants, because of general poor efficiency of the machines used, and sulphur dioxide, because of toxicity, are seldom used today in the United States and Canada. In fact, their use in refrigeration is prohibited by law in most U.S.A. localities.

Sometimes design considerations provide for the use of a 'brine' as a *secondary refrigerant*. At temperatures not far below freezing, a salt solution such as calcium chloride is suitable and, for lower temperatures, organic fluids such as a glycol in the form of ethylene glycol may be used. For still lower temperature extremes where viscosity becomes a factor, trichlorethylene is selected.

Evaporator Vessels

In the preceding section, the means used for removal of the water from the product to be vacuum-dried have been discussed. It is necessary to place the material for drying in some type of vessel, known as the evaporator vessel. Various designs are used, some suitable for batch operation and some for continuous operation. A suitable vapour line connection to the condenser and/or other pumping means must be provided. The size of this vapour connection is critical. The lower the temperature of the product specified for drying, *i.e.* the higher the vacuum, the larger is the diameter of the pipe. The actual dimension of the latter is obtained from calculations based on the established laws of flow for the appropriate pressure range.

Shelf-Dryers are widely used in batch operation, see Fig. 1. The dryer illustrated is entirely of

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welded-steel construction and the shelves supporting the material to be dried are hollow fitted with internal baffles. A heating medium is passed through the shelves which may be water or another liquid circulating at the required temperature or alternatively it may be steam at pressures as high as 150 psi or more.

Shelf-dryers may be used for drying solid substances, slurry or frozen material. In the latter case, modifications are required, particularly for drying pharmaceuticals and biologicals, in order to ensure

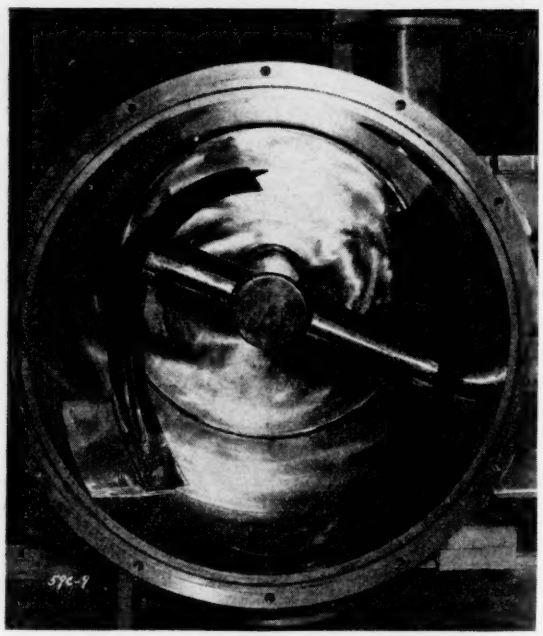

Fig. 3. Interior blades in rotary dryer.

permanently aseptic conditions, especially where the processed material is an injectable, like an antibiotic or hormone.

Pan-Type Vessels are suitable for fairly heavy slurries or other wet material which can be mixed and are suitable for batch drying. These pans may or may not be fitted with blades for mixing or scraping during all or part of the drying operation. A jacket for water or other liquid or steam is placed around the vessel, but at times surrounds only the lower portion of the vessel.

Rotary-Dryers are used extensively and continue to displace vacuum pans in most operations, see Fig. 2. This apparatus may be fitted with revolving blades of various shapes and sizes. Some are arranged with a close clearance between dryer wall and blades to provide scraping action, as shown in Fig. 3. Others have a large clearance to avoid scraping, and a third group contains semi-movable parts producing a tumbling action in addition to the ordinary mixing action. The selection is based on the physical nature of the material, such as its tendency to form clumps, to stick to the chamber walls, or any other significant property inherent in the particular composition being dried. Both the rotary-dryer and the vacuum pan, are suitable for batch drying only and for operation at temperatures above freezing point. The rotary-dryer is jacketted along the whole length of its walls for the circulation of the heating fluid. In some cases, it is necessary to arrange for additional jackets on the heads at the two ends of the dryer.

Rotating dryers are similar to rotary-dryers except that the entire dryer rotates on its longitudinal axis. Fixed or movable scraper blades, tumbling ribs or other mixing means may be included inside the dryer. This type of evaporator is more suitable for slurries which, as dryness is approached, become powdery without passing through a stage in which they become gummy or form clumps. It has the advantage of providing best conditions for a rapid rate of heat transfer from the jacket to the material being dried, but it is limited in the versatility of its application because of the narrow range of materials having the necessary physical properties. The arrangement of the jacket on the rotating dryer is essentially the same as on the rotary-dryer. However, it is necessary to arrange for the vapour connection to pass through the interior of the rotating shaft which supports the dryer, see Fig. 4. This type of design may add to the cost of construction as compared with the rotary-dryer.

Drum Dryers are also used. These have the advantage of providing rapid heat transfer to the materials spread in a thin film over the rotating drum, but

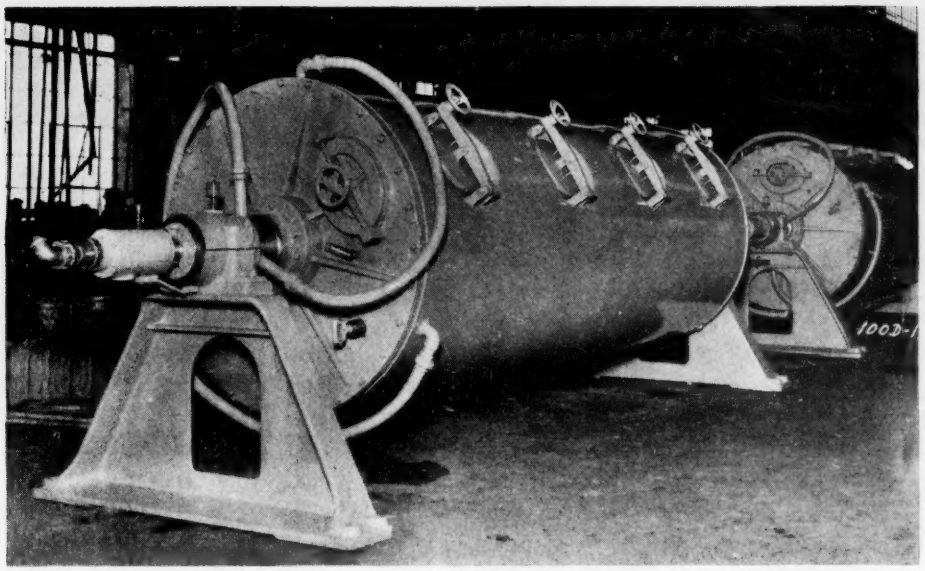

Fig. 4. Two rotating dryers ready for test.

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the film in this case passes over the exterior surface of the drum, and the drum is heated from within by hot liquid or steam. Fig. 5 shows a double (laboratory) size drum dryer, and Fig 6 a single drum dryer. The drums illustrated are designed for drying at atmospheric pressure and are only shown in order to illustrate more clearly the general arrangement. For vacuum drying on a drum, all that is necessary is to provide an outer case fitted with a vapour connection, means for feeding the material through a pipe and means of discharging into a vacuum lock. As can be seen, details of construction for feeding and discharging become more elaborate and expensive. The choice of a single drum or a double drum dryer depends entirely upon the nature of the material. In the case of the double drum dryer, the material is fed into the trough between the two drums and transferred from there

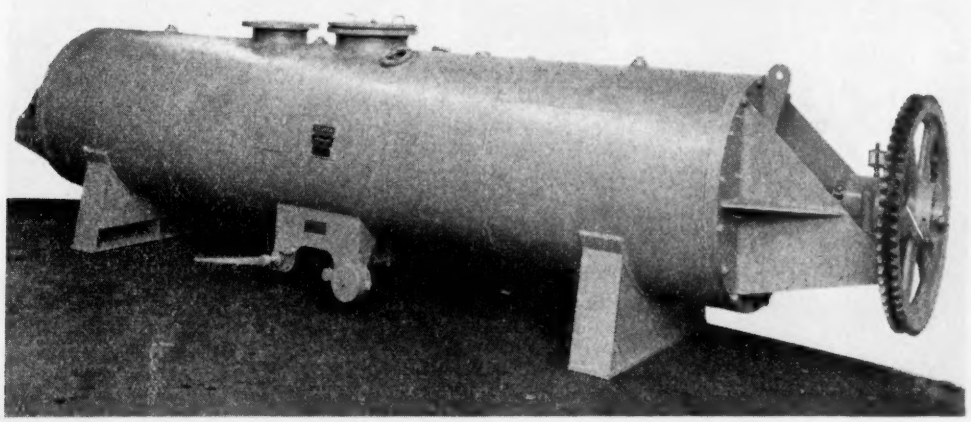


Fig. 2.
Rotary dryer.

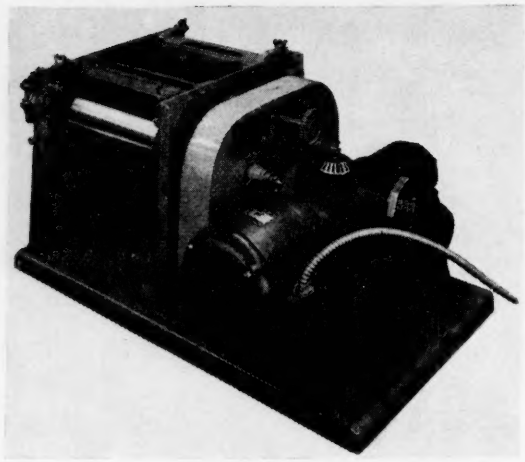


Fig. 5. Laboratory-size double drum dryer—atmospheric.

to the drum surfaces. As the drums continue to revolve, the dried material is scraped off at a point below. Vacuum drum dryers are not used extensively, mainly because vacuum drying is applied to relatively heat-sensitive materials and the essential advantage of the drum arrangement is a rapid heat transfer from a very hot surface. It is true that evaporation has a cooling effect but, nonetheless, fine temperature control is not as readily achieved in this case as in other forms of evaporators. They are however, inherently continuous in operation.

Belt Dryers. Chambers incorporating belts from which the material evaporates also provide for continuous vacuum-drying, an example of which is illustrated schematically in Fig. 7. They may be applied for drying liquids and semi-solids as well as solid foods, chemicals, biological products and other pharmaceuticals. However, in the case of the latter products, other requirements prevent the wider use of the same. Close small size batch control for sterility, potency, and other factors is necessary and, in most countries, small batch runs are man-

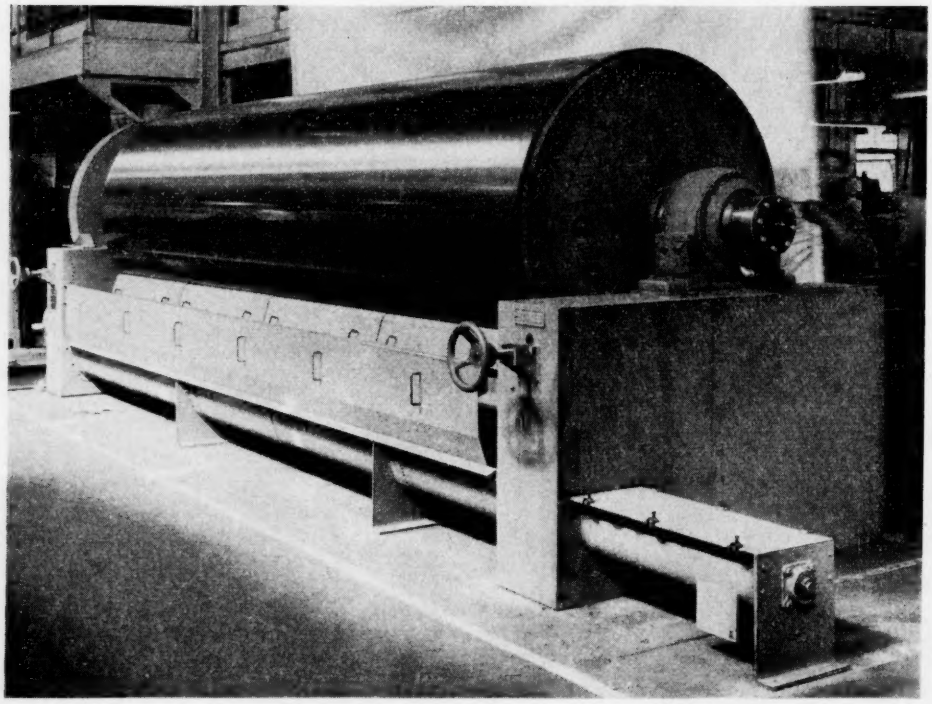


Fig. 6. Single drum dryer—atmospheric.

datory by law. This condition places a limit on the extent to which continuous vacuum drying may be applied.

Fig. 7 shows by way of example liquid concentrate to-be-dried, introduced into the feed pan and applied to a continuous belt of stainless steel by the feed roller. The stainless steel belt conveys the material under a bank of radiant heating elements around the heating drum and past additional heat sources at the top of the unit. Controlled heating during the drying process is effected in a series of stages to maintain maximum evaporation rate commensurate with the drying characteristics of the material. After drying, the product passes over a cooling drum where its temperature is quickly reduced in order to facilitate removal from the belt and to prevent loss of flavour and other desired properties. The dried product is removed from the belt by an oscillating doctor blade. A reversible screw conveyor carries the product laterally to either of two product receivers, which can be filled alternately, and which can be disconnected from the dehydrator without interrupting operation.

As the plant works fully automatically, a minimum of labour and maintenance is required. Either a condenser, a steam ejector, or any of the means discussed for removal of water vapour and non-condensables may be applied in this type of unit. Where economical conditions of cooling water and steam permit, steam ejector operation, by its inherent nature of direct pumping, is a suitable auxiliary to the continuous-belt type of evaporator.

Fig. 8 shows a unit installed under normal commercial production conditions. The same unit is illustrated in Fig. 9 with the door at the end open, exposing the stainless steel belt. Fig. 10 demonstrates the ease with which the dehydrated product is collected in removable drums.

Fig. 11. shows a continuous evaporator using a belt for producing soluble coffee at the Holiday Coffee Corporation. Coffee concentrate is sprayed on a belt of stainless steel moving horizontally. Vacuum is maintained by means of multi-stage steam ejectors. Water removal is accomplished by means of a refrigerated lithium chloride adsorption column. The dry product is passed through an air lock into a hermetically sealed container shown in position under the left hand dryer. In this way it is possible to operate for long periods of time without shut-down or opening to the atmosphere.

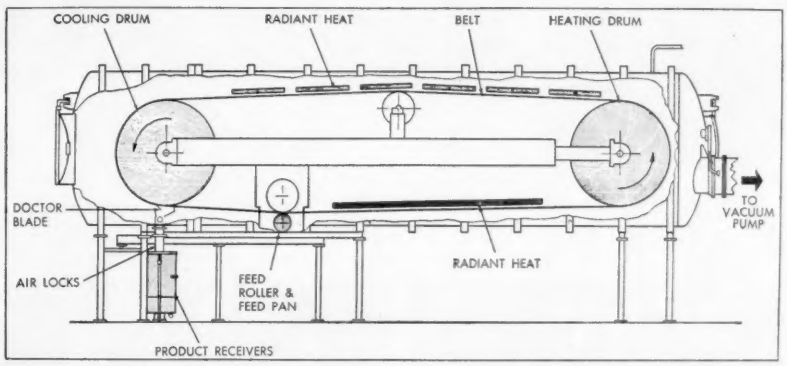
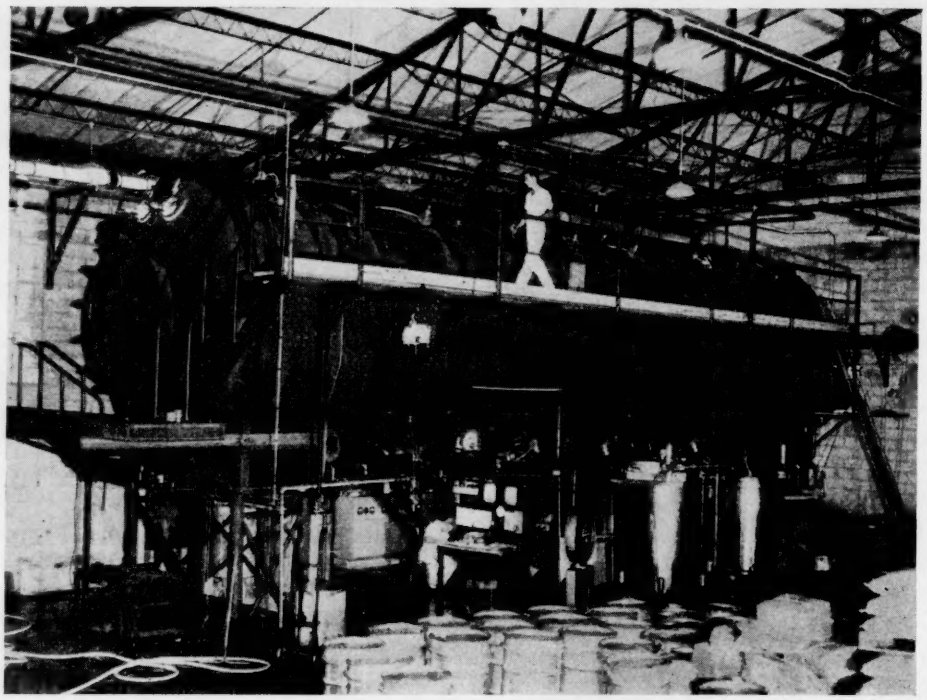


Fig. 7. Schematic arrangement of continuous belt vacuum dryer.

(by Courtesy of Mr. W. Conley, Res. & Dev. Div., Chain Belt Co.)

Evaporation Techniques

'*Multiple Effects*'. Tubular and jet evaporators are used for evaporation, the former from a tube nest, in conjunction with a vapour separator and a condenser. Either of these arrangements may be designed to provide for steam economy by operating in several 'effects.' For example, in a double-effect evaporator the temperature in the first effect may be 135°F and 100°F in the second effect, employing a heating medium at 165°F in the first effect. The vapour from the first effect is utilised for heating in



(by Courtesy of Mr. W. Conley, Res. & Dev. Div., Chain Belt Co.)

Fig. 8. Continuous evaporator with belt.

Fig. 9. Continuous evaporator showing stainless steel belt.

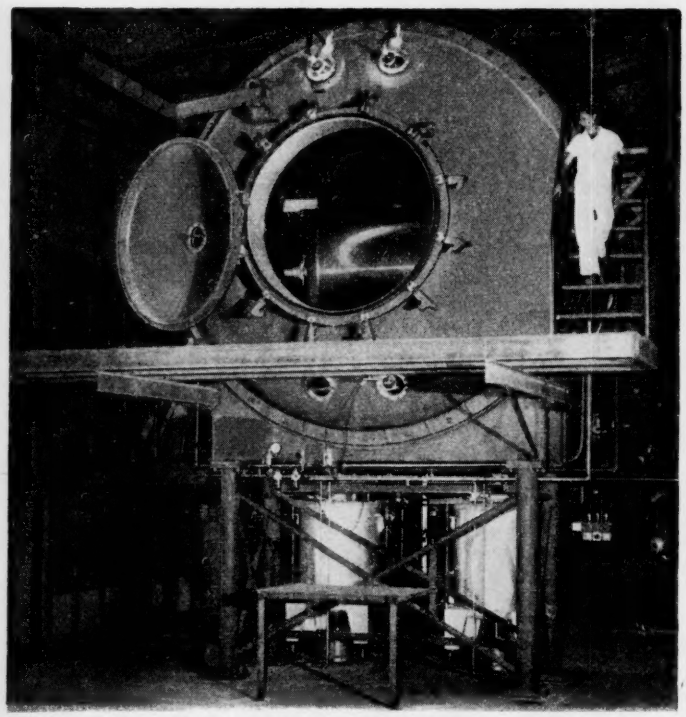
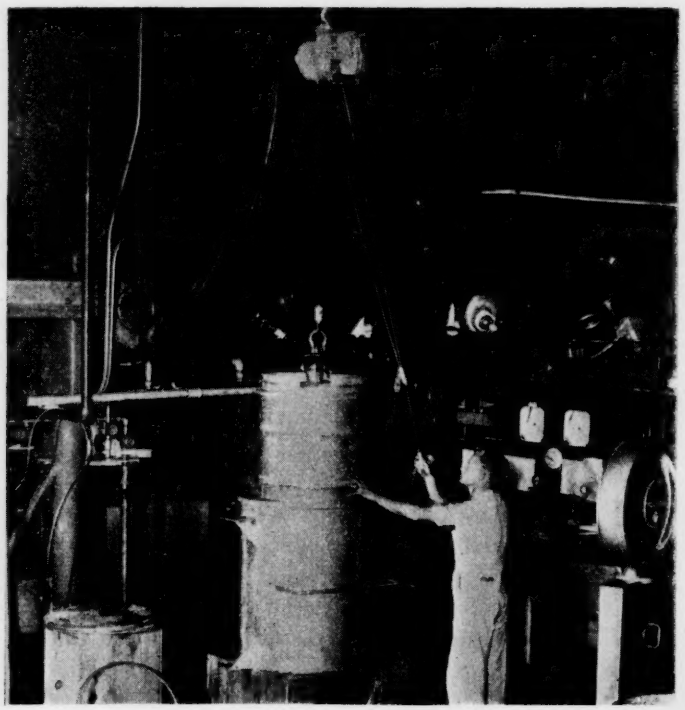


Fig. 10. Collection of dry product in removable drums.



the second effect. Further, the evaporator may be arranged for several stages in each effect. Each stage may operate independently so that the product passes automatically from one stage to the next. In this way, the products of higher densities can be evaporated continuously at the maximum rate of evaporation in each stage. A special separator may be used to minimise entrainment.

column which separates the esters from the condensed water. The essence collects on an ammonia-cooled condenser kept at 35°F. Concentration of the grape juice may be proceeded with until 50 to 60% solids content is obtained, the higher concentration being used in the manufacture of jams and jellies.

Primary and Secondary Recompression. It should be recognised that the number of B.T.U.'s in, for

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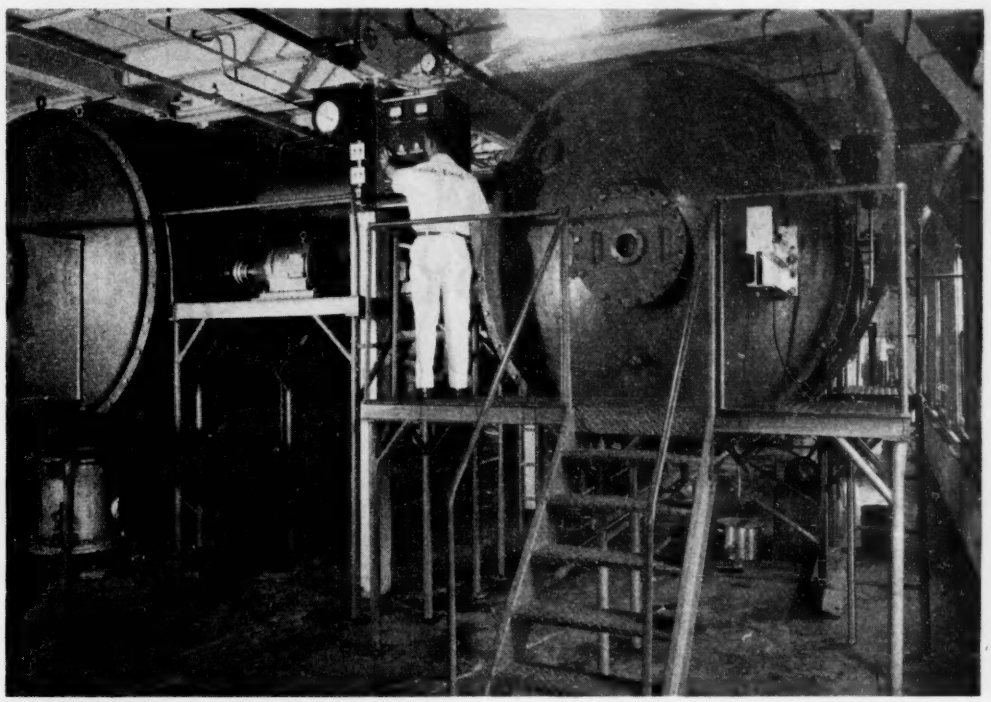
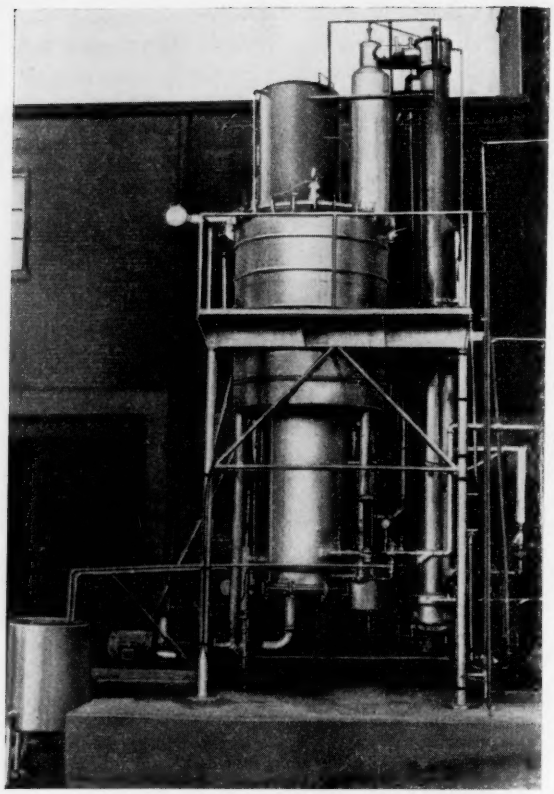


(by Courtesy of Mr. J. H. Durant of National Research Corp.)

Fig. 11. Continuous belt dryer. Hermetically sealed container for removal of dry soluble coffee through an air lock is shown in position under the left hand dryer

Fig 12 illustrates a single effect three-stage evaporator used for grape juice concentration. This evaporator is also equipped with an 'essence recovery system.' The unit is fitted with a preheater to take the juice to 212°F. From here it passes directly into the flash vaporiser where approximately 30% of the total water in the juice is evaporated. Then, the juice passes through a vapour separator which removes the vapour containing the essence. The latter is admitted to a fractionating

example, a pound of steam at 100°F is only about 2% greater than in a pound of steam at 60°F. When water is evaporated from the processed material, the total amount of heat in the vapour leaving the material equals the total amount of heat applied in the evaporator. In many cases, the only difference between the motive steam introduced and the vapour produced is a small difference in temperature and pressure, which can be readily restored by compressing the produced vapour. A thermally perfect



(by Courtesy of Mojonnier Bros. Co.)

Fig. 12. Single-effect three-stage evaporator.

compression system, if such a system were possible, could raise one pound of water vapour from 60° to 100°F by the expenditure of only 18 B.T.U. of energy, *i.e.* less than 2% of the energy latent in that vapour. Even if an only moderately efficient system of compression could be devised, the vapour produced could be compressed and re-used, and only a very small fraction of the energy now necessary for evaporation would be required in such a recompression system.

Use of this recompression principle has been made in direct recompression stills operating at high temperature, but at low temperature the volume of water vapour is so great when operating at normal evaporation temperature that huge, inefficient and expensive recompression equipment is needed. In most cases, the savings actually made in motive steam is more than offset by the friction losses, maintenance and carrying charges upon the large investment necessary. Therefore the problem has been approached in a different way. Instead of attempting to compress the large volume of water vapour direct, the heat from the water vapour is first transferred to another vapour which has the characteristic of a low specific volume, and this low volume vapour is subsequently compressed. This method is known as evaporation by indirect thermo-compression, *i.e.* by secondary re-compression.

For example, in recent plant for the concentration of orange juice, the water evaporates at 75°F. At this temperature, water vapour has a volume of 740 cubic feet per pound. The latent heat of this vapour is transferred *via* a heat exchanger to anhydrous ammonia, boiling at 64°F, and while the water vapour condenses in the shell, the ammonia vaporizes in the tubes. The net result is 2 pounds of ammonia at 64°F instead of 1 pound of water vapour at 75°F, but the volume of the ammonia is 4.25 cu.ft. instead of 740 cu.ft.

It is uneconomical to compress 740 cu.ft. of water vapour from 75° to 108°F in order to recover 1,050 B.T.U. of heat but the compression of 4.25 cu.ft. of ammonia from 64° to 108° in order to recover the same amount of heat is sound, practical, and has been made possible in well-developed commercial equipment. In such plant the motive steam in the tube nests is replaced by ammonia vapour, and the latter is condensed to a liquid just as the steam is condensed to water in the usual evaporator. The ammonia is then cooled to 64°F by expansion and piped to the surface condenser. In the surface condenser, the action is reversed:—The waste vapour is condensed at 75°F and the ammonia vaporised at 64°F. An ammonia compressor is used to compress this vapour from 64° back to 108°F for re-circulation through the evaporator.

The compressor, of course, consumes power. The actual amount of power consumed per unit of evaporation depends on the size of the surface area available in the exchangers. Doubling the area of surface will approximately halve the power needed.

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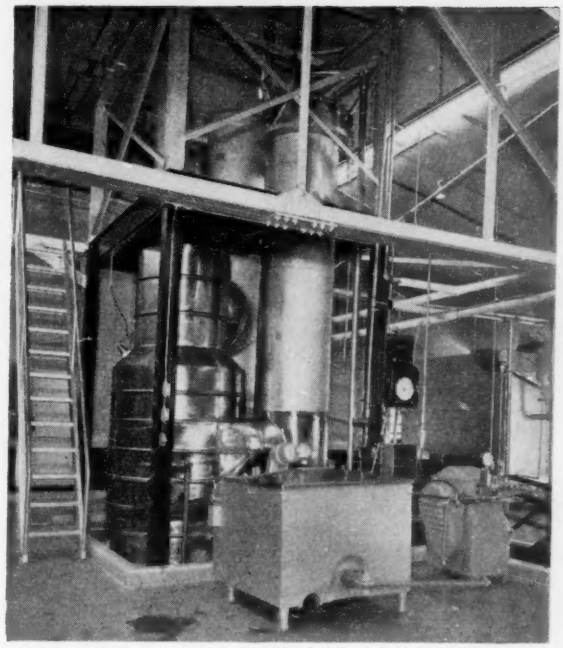
Assuming that the heat transfer coefficients have been established accurately, the determination of the optimum area of surface to be employed becomes a matter of balancing the cost of increased surface area against savings in terms of power usage and compressor size. In recent installations, the power economy curve and the equipment cost curve crossed at about a 100 pound to 225 pound ammonia compression ratio. At this point the power used is 45 h.p. per 1,000 pound of evaporation.

A diesel engine will produce 1 h.p. per 0.4 pound of fuel oil used and 45 h.p. per 1,000 pound evaporation will require 18 pound of fuel oil per 1,000 pound of evaporation. This same 18 pound of fuel oil, burned in a steam generator, will generate about 250 pound of steam, and this steam used in a well-designed and efficiently operated *quintuple effect* steam evaporator will yield about 900 pound of total evaporation. Fig. 13 illustrates such an evaporator which is in operation at Townley Dairy, Oklahoma City, U.S.A.

Engineering Details. A flow sheet, see Fig. 14, shows a four-stage, double-effect evaporator. Kelly and Schwarz have pointed out that falling film evaporators are generally designed to transfer heat for the production of vapour and not for the purpose of sensible heating. Also, in order to avoid temperature differentials caused by excessive pressure drops, it is necessary to provide passage ways for the vapour which are of a large diameter in order to keep the vapour speeds low.

This particular unit is coupled with an existing refrigeration system capable of condensing 13,000 pound of water vapour per hour at 54°F saturation. The economy present in a double-effect arrangement is demonstrated by the fact that the total evaporation becomes 26,000 pounds of water vapour per hour. Although the units are interconnected in such a manner that there are two double-effect systems (A and B), they were not designed or intended to be operated separately. If operated separately, either system alone would have less than half the capacity of the whole plant because the Brix range and sensible heat balance would be different.

Designing the units for a specific operating condition allowed savings in capital cost. The 'A' system operates with 16° Brix concentrate in the second effect and 30.4° Brix concentrate in the first. This results in higher heat transfer coefficients than would be obtained in a normal double-effect design and allows a sizeable reduction in heat-transfer area. The 'B' system operates with 21° Brix concentrate in the second effect and 55° Brix concentrate in the first. These latter Brix ranges correspond to normal double-effect design.



(by Courtesy of Mojonnier Bros. Co.)

Fig. 13. Water vapour—secondary refrigerant recompression evaporator.

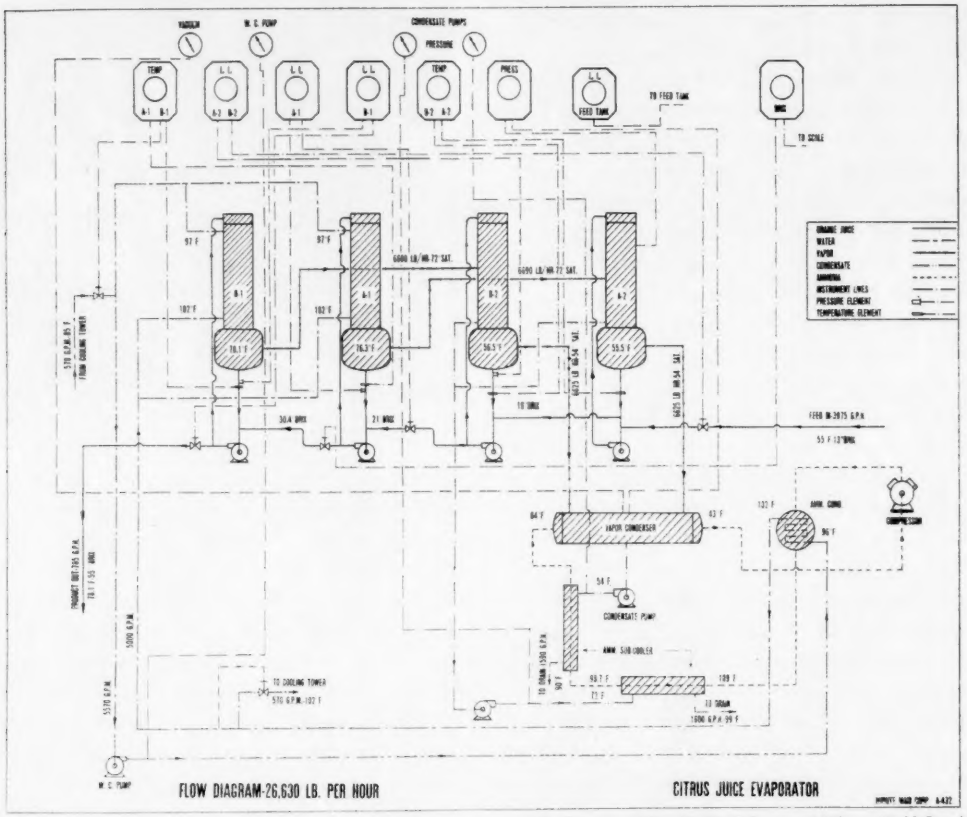
Kelly and Schwarz state that four-stage design presents certain hazards with regard to hygenic conditions in processing. However, a design for three stages results in such extremely large units that the construction difficulties become burdensome. A compromise was made by specifying conditions of equal evaporation in the two second-effects and correspondingly in the two first-effects. This facilitates standardisation of the separation chambers, which reduces the building cost.

A photograph of the same unit is shown in Fig. 15

and Fig. 16. In this latter picture the cylindrical scraper type of condenser can be seen, driven by a motor mounted above it at the top near the roof of the chamber. This arrangement provides for low-temperature condensation of the vapour as ice.

In the production of food, it is important to give careful attention to hygiene. In actual fact, this is largely controlled by regulations established by law. It is important that the equipment be designed to permit ready access for washing down all parts with which the food comes in contact. In addition, pressure-steam sterilisation is highly desirable and, indeed, in many localities it is insisted on at prescribed intervals.

In all evaporators, latent heat of evaporation must be supplied by one means or another. Generally, in all vacuum-drying this is effected by a heat exchange fluid. Water is the most common fluid and steam, at an appropriate temperature and pressure, is convenient in many applications. For low temperature work a non-freezing liquid is required. Depending upon the operational temperature, a suitable mixture of ethylene glycol and water, methyl cellosolve, or trichlorethylene is used. Viscosity is an important factor to be considered not only with regard to liquid circulation but also



(*by Courtesy of Dr. H. W. Schwarz of Minute Maid Corp.*)

Fig. 14. Citrus juice evaporator.

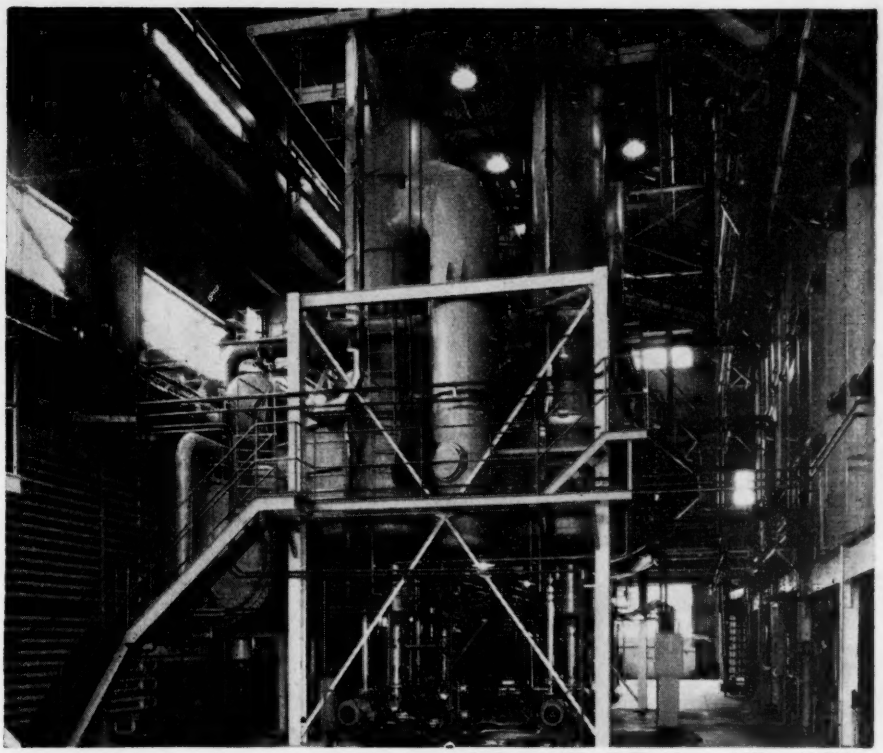


Fig. 15. Four-stage double-effect citrus evaporator.

(by Courtesy of Dr. H. W. Schwarz of Minute Maid Corp.

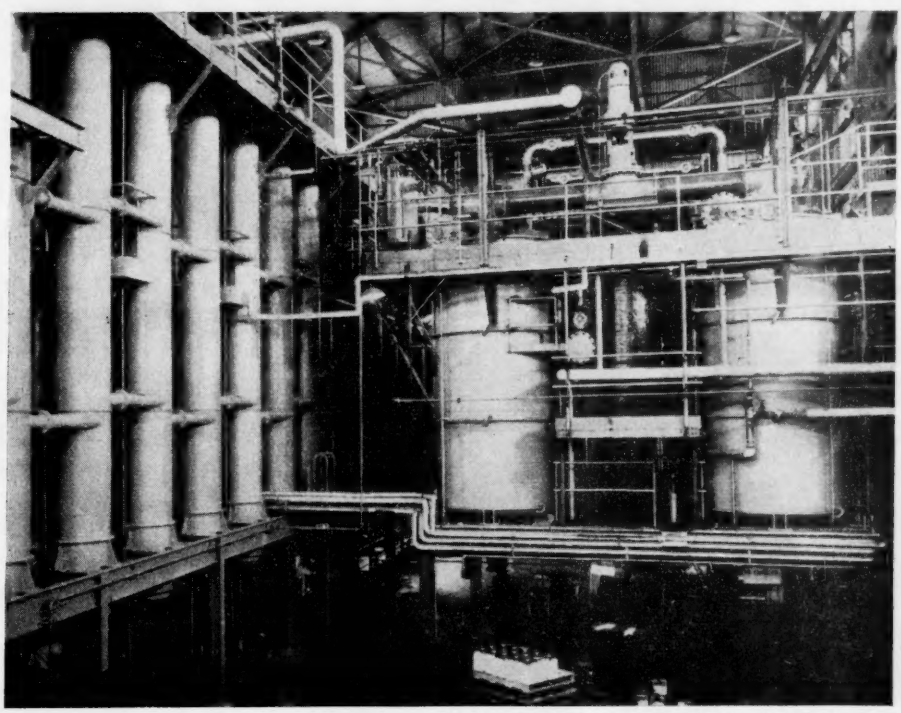


Fig. 16. Four-stage double-effect citrus evaporator showing refrigerated vapour condenser.

(by Courtesy of Mr. J. H. Durant of National Research Corp.)

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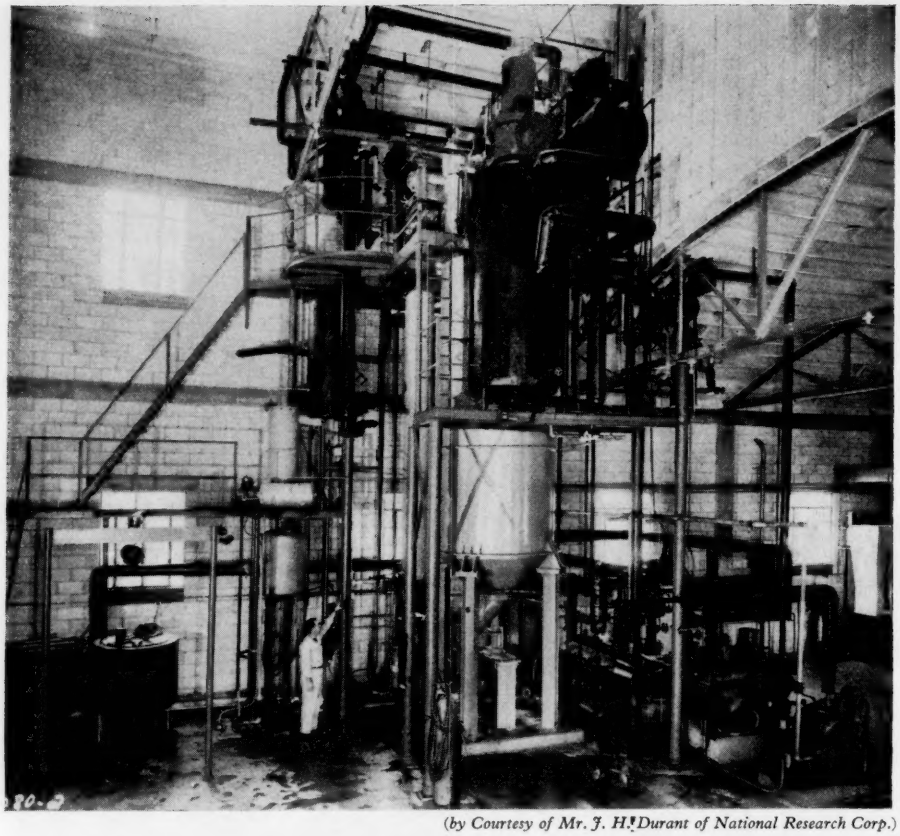

Fig. 17. Pilot orange juice freeze dryer (no longer in operation).

(by Courtesy of Mr. J. H. Durant of National Research Corp.)

in order not to interfere with proper heat transfer at the exchange surfaces. In freeze drying, the heating medium may be below 32°F for part of the cycle, particularly when treating certain vaccines. The transfer of the heat to the product within the evaporator is effected by coils and/or jackets. Radiation from either a low temperature black radiator or some hotter source, is also used. Induction heating at various frequencies, including radio high frequency, has been proposed but has not been applied in practice.

Vacuum Gauges

Almost any reliable type of vacuum gauge may be used as long as it is properly selected for the range of pressures in question. At pressures above 10 or 20 mm. Hg an ordinary closed-end manometer will generally be of sufficient accuracy but, of course, it is a fragile instrument. A mechanical type such as the Bourdon gauge can also be used, but it is important to recalibrate it properly from time to time. At lower pressures, the McLeod gauge of course is the ultimate standard, provided that proper means are used for avoiding errors caused by the presence of condensables within the gauge during operation. Such gauges are suitable for use over the entire range from 50 mm. Hg down to a fraction of a micron Hg. In the relatively high pressure range, say, above about 1 micron Hg, a built-in chemical trap provides the simplest method of protection against condensation errors and permits measurement of the correct total pressure, including water vapour. It consists of a glass tube large enough in diameter to cause no undue restriction to the flow.

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The tube is filled with a chemical having a vapour pressure well below the minimum pressure to be encountered in the high vacuum system. This prevents vapour from entering the gauge. By a suitable choice of the chemical, vapours other than water (such as alcohol and oil, which would cause errors similar to those originating from water vapour) can be trapped. A colour indicator chemical can be employed to warn when the trapping agent must be replaced.

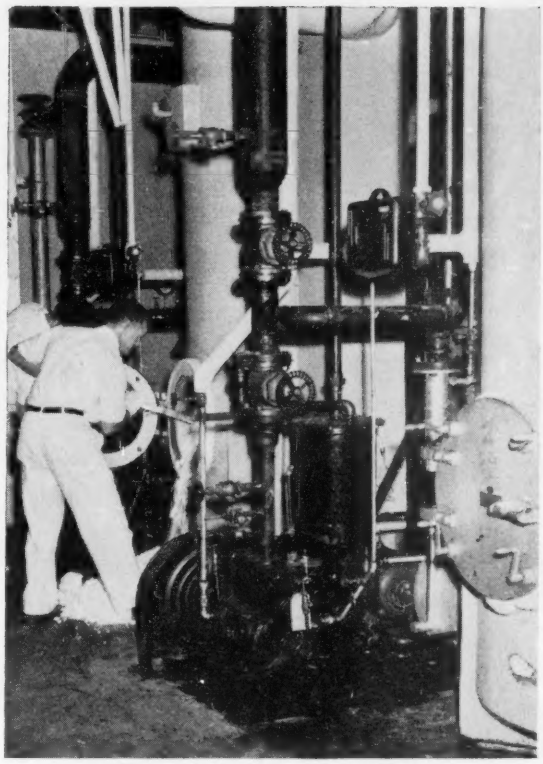
The chemical trap causes the measurement of true total pressures, including that of water vapour, not just the pressure of non-condensables only. Although there is only dry air in the indicating tube at all times, this air is present at a pressure which exactly balances the *total pressure of condensable vapour and air* in the system on the other side of the trap. This has been proved experimentally by measuring the vapour pressure of ice at various known temperatures under accurately controlled conditions.

As long as total pressure is below the condensation point, condensation cannot occur and accurate readings are obtained. Water vapour originating in the glass or mercury of the gauge, however, may not be pumped away thoroughly enough to establish equilibrium with the system, in which event a fictitiously high reading will be obtained. Generally, this occurs at pressures below 10 micron Hg, but can be avoided by drying the gauges. A McLeod gauge fitted with a vapour trap automatically provides protection against this type of error.

Many other gauges are available which, for continuous indication or recording, operate in response to some property of the atmosphere in the vacuum system such as thermal conduction or ionisation of the gases. Most of these require periodic calibration against a McLeod gauge where high accuracy is essential.

FREEZE-DRYING

The pumping equipment for non-condensables and for water vapour is broadly speaking the same as used for vacuum drying but is selected to meet the specific pressure requirements. The pressure range varies considerably from product to product. For many foods, a pressure of around 2 to 3 mm. Hg is sufficiently low, whereas, for blood plasma, for instance, 500 micron Hg is the optimum with respect to the maximum temperature of the product permissible. Other products such as viral vaccines require lower temperature and hence lower pressure and with some a final blank-off pressure of 0.5 to 1.0 micron Hg is necessary to attain proper lower residual moisture without excessive heating. In preparation of specimens for histo-chemical studies with tissue and other biological materials considerably lower temperatures are needed to prevent eutectic changes in the molecular arrangement.



(by Courtesy of Mr. J. H. Durant of National Research Corp.)

Fig. 18. Removal of ice from rotary condenser receiver.

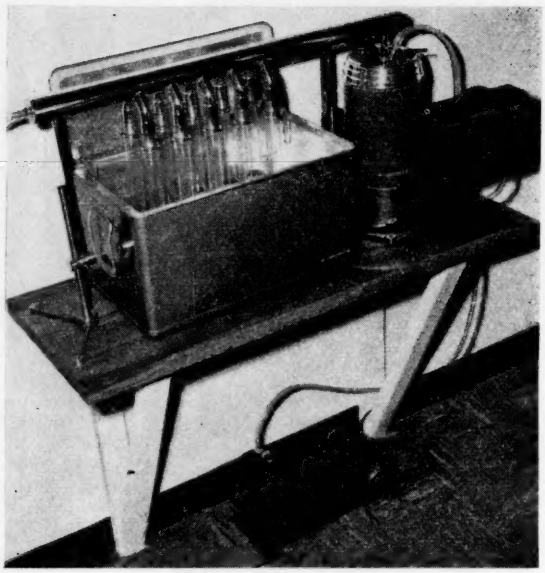
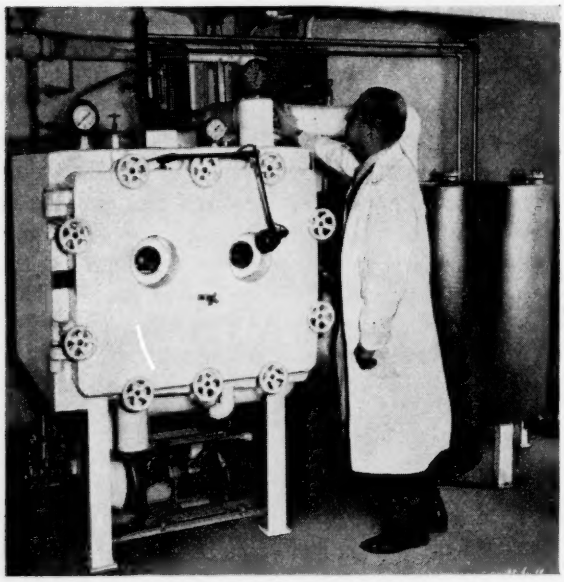


Fig. 19. Tissue bank dryer as used for arteries, skin and bone.

Fig. 20. Dry ice chamber-type freeze dryer installed at the Philadelphia serum exchange.



Pressures as low as 0.01 micron Hg are used in some applications.

Obviously, as far as mechanical pumps are concerned, reciprocating types do not reach the freeze drying band of pressures, but single-stage rotary pumps are suitable. For the lowest range of pressures required in the applications mentioned earlier, oil booster pumps and, in some cases for histochemical work, diffusion pumps are employed. Four- and five-stage steam ejectors also have been used but not widely.

The water vapour may be removed by freezing out with cold condensers or by direct pumping, particularly where four- or five-stage steam ejectors are operated. If the steam ejector is used for removal of the water vapour, as well as non-condensables, the capacity must be adjusted accordingly.

The condensers may be ordinary coils through which a refrigerant is circulated, or coils having fins in order to extend the surface for the sake of greater efficiency, or they may be flat plates or cylinders. In the case of cylinders, they may be immersed in a cold bath or surrounded by a jacket through which the refrigerant is circulated. This type of condenser may also be fitted with an internal scraper for the continuous removal of the ice which is allowed to fall into a lower refrigerated reservoir. In Fig. 17, such a rotary condenser is shown at the top of the ice receiver below it. This particular unit has a 25-pound per hour capacity. At the bottom is a vertical dryer. This installation is for dried orange juice as installed in Florida.

In Fig. 18, a similar unit is at the stage shown where the powdered ice is removed from the receiver. On the extreme right is a duplicate ice receiver with the door closed. A rotary pump is mounted on the floor between the two condensers and a 'swivel' McLeod gauge above it.

Dry-ice may also be used in place of Freon and ammonia refrigeration. Operating costs are much higher, but equipment costs are the least. Where such equipment is to be used only temporarily or for short periods, this is the smallest total investment. The dry-ice condenser may be immersed in a bath as in the tissue dryer illustrated in Fig. 19 developed

by the author in collaboration with Dr. G. W. Hyatt CDR(MC), of the U.S. Naval Tissue Bank, Bethesda, Maryland. Another arrangement is illustrated in Fig. 20. The condenser is on the right and is constructed of stainless steel with an internal well into which the dry-ice is placed along with a fluid such as methyl cellosolve or alcohol. The 5-inch 'jacket', with sight glasses at the top, provides the vacuum space connected with the drying chamber on the left. The ice collects inside this jacket on the inner wall.

The evaporator vessels used may be so-called 'shelf-dryers' suitably designed to provide for proper sterilisation, as well as providing the larger vapour line required for the low pressures used in freeze drying. Also, modifications may be made for proper sterilisation in food drying, and asepsis when processing medicinals, as well as provisions for the incorporation of a complete refrigeration 'package'. Fig. 22 illustrates a freeze-dryer incorporating a 'package' arrangement. Heaters for the heat exchange medium and all other equipment required

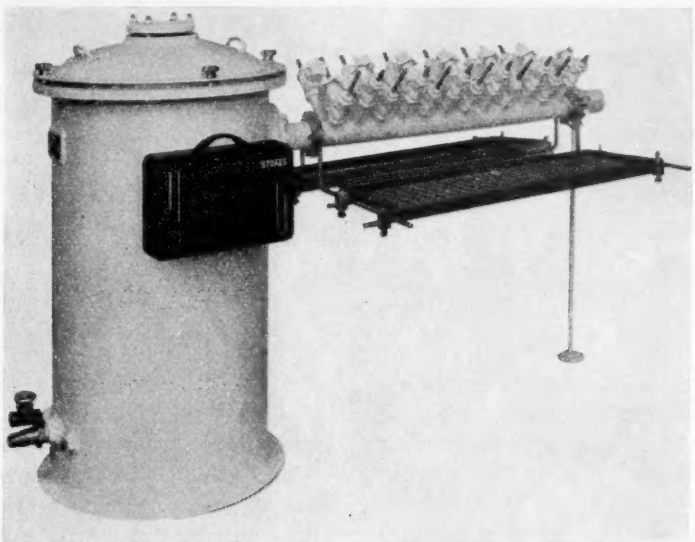


Fig. 21. Freeze dryer with chemical-desiccant tank fitted with a manifold.

In place of freezing out, the water vapour may be collected by means of a suitable chemical desiccant. To ensure proper low vapour pressure at the end of the drying cycle, the chemical should be one forming a fixed chemical hydrate such as calcium sulphate and not one of the adsorptive type like silica gel. The latter is quite suitable for dehumidification of air circulated through a cylinder in the area where the equipment is installed or for bringing up an evacuated chamber to atmospheric pressure with dry air but it is not suitable when present within the vacuum system itself for the purpose of keeping overall vapour pressure at a minimum. This type of unit is illustrated in Fig. 21.

are mounted below and around the chamber. Internal condensing plates are provided which allow rapid and unimpeded flow of the vapour from product to condenser.

In freeze drying where low temperature condensation is used, a large surface is essential for efficient operation. Also, proper ice-holding capacity must be provided together with means for removal of the ice by melting or otherwise. A novel method of effecting the latter consists of the simple measure of melting the ice layer immediately adjacent to the condenser plate surface where upon the entire block of ice can be easily slipped out of the condenser through the door. This minimises both the time

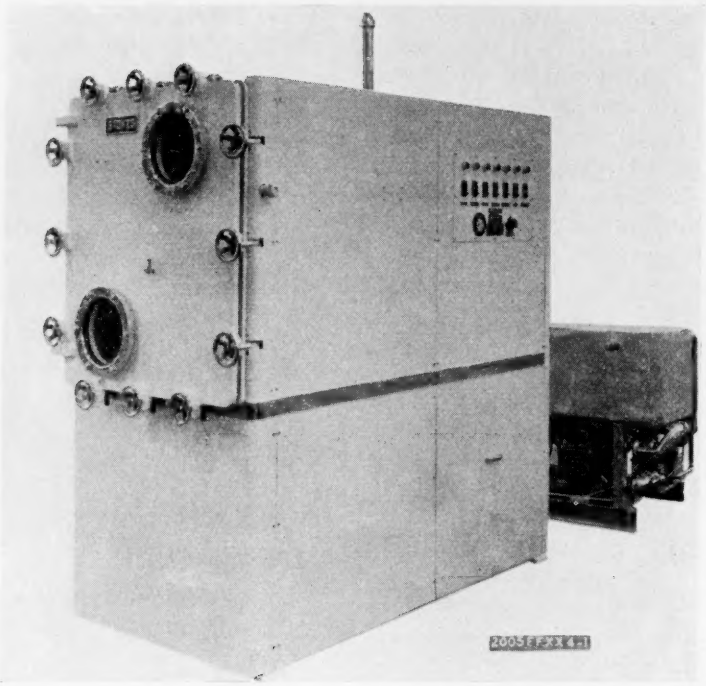


Fig. 22. Complete 'package' freeze dryer with all accessory equipment incl. condensers, factory-mounted and assembled.

required and the amount of heat needed for complete melting while avoiding complications due to moving parts associated with the use of scraper mechanisms and other mechanical arrangements for the removal of the ice.

Ice depositing on a condenser under the vacuum conditions employed in freeze drying is exceedingly dense. This has the beneficial result that its thermal conductivity is greatly in excess of atmospheric frozen ice, which explains why condensers work so efficiently even after a relatively thick layer has built up. However, large surfaces are needed to permit proper heat transfer from the refrigerant to the condenser and also for transfer of the latent heat of condensation to the condenser surface.

In laboratory work, manifolds are widely used, as evaporator vessels and bottles, test tubes, or other types of phial, containing the product are attached individually for treatment. One of these is illustrated in Fig. 19, and another form in Fig. 21. Sometimes the nipples for connecting the bottles are placed around the periphery of a dry-ice condenser or chemical tank. Other modifications, arrangements and forms are legion.

Fig. 23 shows an experimental small-scale dehydration unit containing provision for heating and pumping-down as well as vacuum gauges and the controls for the mechanical pump. The unit operates at pressures down to 10 micron Hg using only a gas ballast mechanical pump which handles the water vapour load and ultimately discharges it to the atmosphere without contaminating the pumping oil, thanks to the gas ballast principle.

Dr. R. I. N. Greaves developed a novel method of 'Centrifugal' freeze drying. This is applicable particularly to drying fairly large amounts in individual bottles where shell freezing is desirable. The bottles are placed in the vacuum chamber and are spun rapidly so that the centrifugal force spreads the liquid over the walls of the bottles. Vacuum is then drawn and self-freezing as a result of reduced pressure ensues. The centrifugal action also pre-

vents frothing and bubbling during vacuum freezing.

Such a unit is illustrated in Fig. 24. Fig. 25 shows separately the centrifugal plate which in this case is to carry small ampoules.

The British practice is to carry out drying in two operations. The final moisture content of the dried product is brought to the specified figure of 0.5% by secondary drying on a manifold with phosphorus pentoxide as a desiccant. This unit is illustrated in Fig. 26.

PROCESSING OF FOODS

For drying in the belt type of dryer illustrated in Figs. 7, 8 and 9, the liquid concentrate to be dried is introduced into the feedpan and is passed onto the continuous belt of stainless steel by a feed roller. The stainless steel belt conveys the material under a bank of radiant heating elements around the heating drum and past additional heat sources at the top of the unit. Controlled heating during the drying process is effected in a series of stages to maintain the maximum evaporation rate commensurate with the drying characteristics of the material. After drying, the product passes over a cooling drum where its temperature is quickly reduced to facilitate removal from the belt and to prevent loss of flavour and other desired properties.

The dried product is removed from this belt by an oscillating doctor blade. A reversible screw conveyor carries the product laterally to either of two product receivers, which can be filled alternately, and therefore can be disconnected from the dehydrator without interrupting operation.

In order to dry milk yielding a concentrate suitable for final processing by spray drying, equipment like that illustrated in Fig. 13 may be used. The milk can be concentrated at a temperature below the body temperature of the cow. Under this condition none of the proteins are denatured. After spray drying the powder is of excellent flavour and of high solubility. This new method offers great possibilities for the future of the spray drying of milk.

Skim-milk can be concentrated in the ratio of about 3 : 1 and can be marketed at this concentration in a refrigerated condition or the concentrate can be used to produce new kinds of dairy products. These new products include skim-milk with a fat content of about 0.5% and with a total solids content of about 12%, as well as a milk product that is being merchandised in U.S.A. in place of 'half milk — half cream'. This new product contains about 12% of milk solids and no fat. Other materials such as insulin, various biochemicals, fruit juices, coffee extract, clam broth and vanilla extract are being dried to a high concentration.

(by Courtesy of Mr. J. H. Durant of National Research Corp.)
Fig. 23. Laboratory bell-jar high vacuum dryer.

In batch operation employing vacuum shelf-dryer equipment the product may be either loaded into the plant after having been prefrozen in separate equipment or it may be loaded unfrozen and vacuum evaporation used for freezing. In vacuum freezing, the temperature drops quickly (within 15 to 30 minutes) from ambient to −35° to −45°C. The heaviest portion of the refrigeration load is obviously spent in reducing the temperature of the heavy steel construction of the chamber rather than the relatively small weight of product placed in the chamber.

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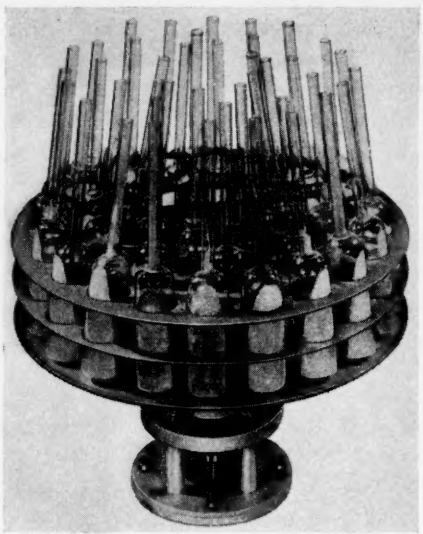
Fig. 25 (right). Loaded single centrifuge plate.



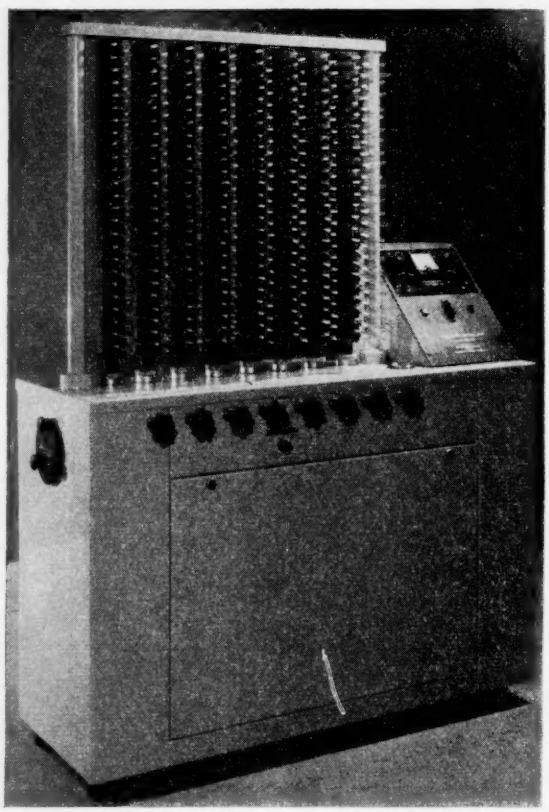


Fig. 26 (Above). Secondary freeze dryer with ampoules in position on the headers.

Fig.. 24 (below). Centrifugal freeze dryer.

(by Courtesy of Edwards High Vacuum Ltd.)

After the chamber has been loaded and the product has been frozen at this low temperature, the high vacuum required is produced. At this stage, the temperature of the chamber must be brought up slowly to about room temperature. With the chambers at this temperature, the product itself, because of the prevailing high vacuum, remains at about −35°C or lower, until all the ice has sublimed to the vapour condenser.

The plates on which the product is supported are hollow so that a suitable heat transfer medium can be circulated. Obviously, uniformity is of first importance. Upon the completion of drying, the material is moved from the dryer for final packaging in a vapour-tight and vapour-impermeable container.

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Dehydrated foods have long been recognised as having greatest stability without the need for refrigeration. This makes for lowest cost of distribution and convenience of storage on the pantry shelf. But never, until now, have commercially dried products been satisfactory to the palate. Freeze-dried foods of highest quality, however, can take to all the savouriness known so far only in the locality of origin of the food. Mouth-watering juicy beefsteaks, pork chops, and even unusual fish dishes made at the seaside to skilful Chef's recipes are now available for serving in a matter of minutes from the can to the table in home or tent. The obvious advantage of no refrigeration for the tropics is clear. Not so clear, however, is the fact that the practical use of frozen foods in cold regions presents great problems for example, in readily defrosting the food by hunters. Warming ovens or other similar means may not be available. Boiling water defrosting does not yield a tasty product in all cases. Who would enjoy a frozen chop or prime steak defrosted in a pot of boiling water before charcoal broiling?

Foods like crab, oyster and clam, and even lobster, mixed with other ingredients, are particularly suitable for this new type of preparation. The cost of the raw material may be reduced by the use of lower priced ingredients to be added. The factory prepared product is made initially by professional technicians utilising fine chef-developed recipes. The product as sold, if consisting of cooked ingredients, is readily prepared for consumption by the simple addition of hot water. Non-cooked products are readily reconstituted with cold water and subsequently cooked according to directions or the consumer's preference.

The manufacture of the freeze-dried product begins in the same manner as that of any product processed by the Frozen Food Industry. In the case of meat, a proper cut must be selected, trimmed free of fat and de-boned for individual servings of the right thickness, and then frozen. Bacterial growth is not only inhibited in the processing stage but also cannot occur in the finished dried product during storage. However, after reconstitution with water, it must be treated like any fresh food.

Almost all food products lend themselves to successful treatment by freeze-drying. However, because of the low intrinsic monetary value of certain foods, many cannot carry the burden of higher processing cost. Such low cost items are carrots and potatoes as compared with high cost lobster and back-fin lump crabmeat. On the other hand low cost products process well, and so may be used with advantage as added ingredients (mentioned before) to foods prepared in accordance with high grade Chef's recipes and yielding greatly enhanced true connoisseur's dishes. At the same time, this has the agreeable by-effect that the overall cost of the expensive ingredients dried and sold is somewhat eased.

A presentation of the actual cost of processing, in simple terms is difficult. First of all, there are differences in cost of ingredients (low where the source of raw material supply is near) and labour cost in various localities. Also, there are varying accounting procedures within a given industry, as well as within a particular company, which affect the allocation of overheads. Generally speaking, power and labour amount to something like 5 cents per pound of water removed, based on conditions prevailing in an average U.S.A. urban community. By assessing cost in this manner, the factor of initial moisture content adjusts itself automatically. Ob-

viously the cost is greater than that for the processing of frozen foods for distribution *per se* because in the case of freeze-dried products freezing is only part of the process. Vacuum-drying has to be added, but operating costs for this are not high. Equipment costs, however, are high, and depreciation is significant. The extent to which this affects costing depends on the accounting practices followed. On the other side of the ledger is lower shipping and storage costs, because the shipping weight is less and refrigerated transport and storage are not needed.

At the present time, the prospects of freeze-dried foods in the consumer market are good and products of unusual quality may reach places not easily reached by distribution of frozen products. On the other hand, at least in the foreseeable future, one could not expect freeze-dried products to displace frozen foods on the U.S. market, but they may well supplement them. There is a definite Gourmet market readily accepting freeze-dried foods; also they may contribute considerably to the enjoyment of picnics. Whole meals may be provided this way, requiring only the addition of just a minimum amount of warm or boiled water for reconstitution, and subsequent serving.

CONCLUDING REMARKS

In conclusion, it can be said that freeze drying food is economically feasible and that a market exists for such products. However, individual ingredients and mixtures should be judiciously selected, and production located where low cost sources of highly perishable raw material are available, be it at home or abroad. In this manner high quality ingredients may be brought to the market representing delicacies available in no other way to the ordinary home market consumer.

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MOLECULAR DISTILLATION

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Summary

MOLECULAR DISTILLATION became an important industry during the past fifteen years, and has enabled many thermally sensitive materials to be prepared on a commercial scale, but the development of stills appears now to have reached a resting-point. After a short introduction, the author discusses in turn the various forms of molecular still existing at the present time, including pot, falling-film, centrifugal, rotary and wiped-film patterns. Each basic form is given a brief historical background, followed by a review in greater detail of developments during the last decade or so. Models incorporating important ideas and modifications are described as fully as possible, and references are given to sufficient numbers of minor variations to present a fair picture of the subject. While theory is introduced as necessary, for example in considering the elimination curve or the assessment of still performance, the main emphasis of the article is on the design and construction of distillation apparatus. As much practical information as possible is given, in order that it may be of use to the laboratory worker or chemical engineer contemplating work in the field. The author concludes that the more general use of molecular distillation in the laboratory might lead to wider application of the process on an industrial scale, but that new designs for low-cost apparatus of improved fractionating power would seem to be needed before there is a major resumption of plant construction.

Sommaire

LE PROCÉDÉ DE DISTILLATION MOLÉCULAIRE est devenue important dans l'industrie depuis les quinze dernières annees, et a permis de préparer à l'échelle commerciale des produits sensibles à la chaleur; mais le développement des colonnes semble maintenant avoir atteint un point d'arrêt. Après une courte introduction, l'auteur discute des différents modèles de colonnes moléculaires existants, tels que colonnes centrifuges, colonnes à film tombant, etc. Un bref rappel est fait sur le développement de chaque modèle ainsi qu'une revue détaillée des développements et améliorations apportés pendant ces dernières années. L'auteur décrit aussi complètement que possible des modèles comportant des idées et modifications importantes et des références sont données sur un nombre suffisant de détails mineurs afin de présenter une image très ressemblante des appareils discutés. Bien qu'il soit nécessaire d'introduire une partie théorique sur l'observation des courbes d'élimination ou le rendement de tels colonnes, cet article est particuliérement orienté sur l'étude et la construction d'apparails de distrillation. Des informations pratiques sont données autant qu'il est possible afin d'aider les ingénieurs et chercheurs voulant s'orienter vers ce domaine. L'auteur en conclusion pense qu'un emploi plus généralisé de la distillation moléculaire dans les laboratoires peut conduire à une plus application de ce procédé à l'échelle industrielle, mais qu'il est necéssaire de fabriquer des appareils bon marché ayant une puissance élevée avant de fabriquer des appareils plus importants.

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INTRODUCTION

MOLECULAR DISTILLATION is a high vacuum process, whereby material distils from an evaporating surface to a relatively cool condensing surface, positioned directly opposite to it, under such an operating pressure that the mean free path of the distilling molecules is greater than the distance between the evaporating and condensing surfaces. The thermal hazard to the material is thus reduced to a minimum.

The method is extremely valuable for the distillation of compounds in the molecular weight range 250–1,000, which have volatilities too low for distillation to occur at practical rates in conventional stills and a structure which is readily damaged on heating. Among these are the fat-soluble vitamins, sterols, glycerides, etc., and many synthetic chemicals, the concentration of which by means of the molecular distillation process—also known as unobstructed-path or short-path high vacuum distillation—has constituted an important industry for the last decade. In commercial practice, processing conditions slightly outside those given in the above definition may be used. Not all distillands are equally heat-sensitive, and it is often possible to use higher distilling pressures than the postulated 'molecular vacuum', or to interpose barriers between the evaporating and condensing surfaces without serious risk of damage to the distilling molecules.

* MS. received June, 1958

The definition of 'mean free path' should be examined critically (Fig. 1). The important path length is that travelled by a molecule of the distillate before colliding with a molecule of residual atmospheric oxygen. Collisions between two molecules of the distillate are usually harmless,[137] although if impact is made at certain angles this may result in one of the molecules returning to the evaporator

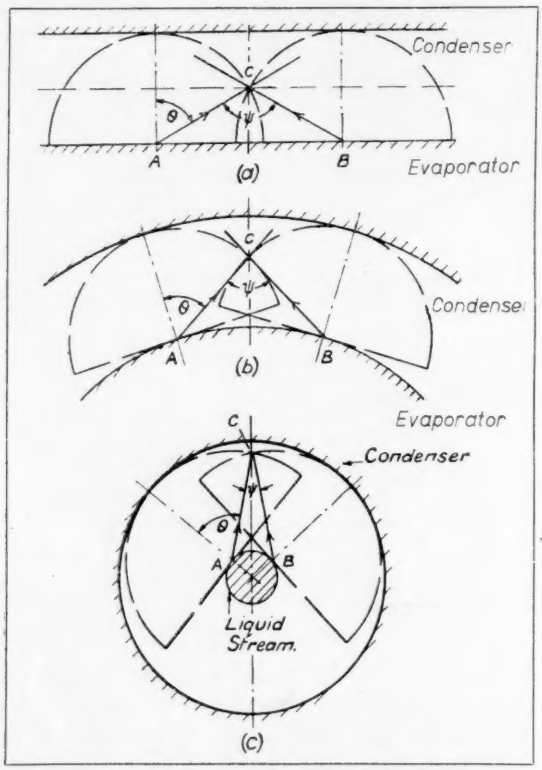

Fig. 1. Comparison of paths of molecules from flat and curved surfaces. ψ—angle of approach between molecules; θ—inclination of molecular path from normal. (*Burrows*)

surface and being subjected to a further period of heating. At a pressure of one micron Hg, the residual gas molecules in a system will have a mean free path of about 5cm. and this represents a typical evaporator-condenser gap in molecular distillation equipment.

Molecular distillation differs in several important respects from atmospheric-pressure or ordinary reduced-pressure distillation. Firstly, there is no boiling-point: Since there is no external atmospheric pressure to overcome, distillation takes place whenever there is a temperature difference between evaporator and condenser. Secondly, there is no ebullition: The very low saturation vapour pressure of the distilland in the range of safe working temperatures is generally insufficient to overcome surface tension and viscosity, and to support bubble formation.

Finally, no azeotropic mixtures are formed in the distilland, no appreciable refluxing occurs at the evaporator surface, and broadly speaking, no interaction takes place between the molecules of the distillate, once they have left the evaporator surface. Most of them will, in fact, travel unimpeded to the condenser and will be collected there. Provided that the rate of re-evaporation from the condenser is small, which in general it will be for most of the low-volatility materials processed in that way, the rate of distillation will be fairly close to the absolute evaporation rate, *i.e.* the rate at which molecules leave the evaporator surface. Langmuir[1] has shown that the absolute rate of evaporation n is given by

$$n = PA\sqrt{\frac{1}{2\pi MRT}}$$

where P = Vapour pressure of the distilland (dynes/cm².)
A = Area of the surface of the distilland (cm².)
M = Molecular weight of the distilland
R = Gas constant
T = Absolute temperature of the distilland (°K)

Thus it can be seen that, under the conditions of molecular distillation, substances with the same $P:\sqrt{M}$ ratio cannot be separated. If a two-component mixture is being distilled, the separation α is given by

$$\alpha = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}$$

Where p_1 and p_2 are the partial pressures of the two components.

In practice, distillation rates are always slightly less than absolute evaporation rates, since collisions between distilling molecules travelling at large angles to the normal may, as indicated before, result in the return of some of them to the distilling surface.

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Burrows[2] has shown that for a collision between molecules coming from two adjacent points on a surface to result in a return of either molecule to the surface, the angle between their paths must exceed a certain limiting value. Hence, when distillation takes place from two points on a curved surface, the number of molecules which are capable of returning to the evaporator as a result of collisions depends on the angle between the normals at the two points. With a convex surface, where the normals at two adjacent points are inclined away from one another, few molecules have the probability of returning. Conversely, with a concave surface the reverse applies, and the mean free path of the distilling molecules is correspondingly reduced.

Articles on the theory of vapour transfer applicable to evaporation under high vacuum conditions have been published by Embree[3], Carman[4], Burrows[2], Hickman[5] and others.[6–9]

The principle of unobstructed-path distillation was first used in 1922 by Brönsted and Hevesy[10], to separate the isotopes of mercury. The technique was further developed a few years later by Burch in England, and Hickman in America, who had been working independently on diffusion pumps and pump fluids and had found that a variety of relatively non-volatile substances could be evaporated at the very low pressures which were attainable with the new pumps. Since then, several distinct types of high vacuum stills have been evolved.

In reviewing developments in the field of molecular distillation, it is proposed to consider these evolutionary forms in turn and to discuss, one by one, the uses and limitations of each principal type. A selection of review articles published previously is given at the end of the paper.

POT STILLS

Working Principle and General Characteristics

Early molecular distillation work was carried out using simple pot stills. The material to be distilled was put into a small flask equipped with a vertical condensing surface in the form of a 'cold finger', and the space inside the flask was evacuated to a pressure of about 1 micron Hg. After a preliminary degassing period, the layer of distilland was heated. The distillate collected on the condenser and was either drawn off into a small receiver or removed by dismantling the apparatus.

Pot stills, see Fig. 2, conforming generally to this pattern were described by various authors [13–17] at the beginning of the 1930's, notably by Burch[11] and Hickman[12], but although the stills were useful tools in research they suffered from several inherent disadvantages, notably, poor fractionation and thermal hazard.

Fractionation Efficiency. Poor fractionation results from the absence of ebullition, which in a conventional still not only increases the effective surface area of the distilland but also ensures thorough mixing. Under high vacuum conditions, where this mixing does not occur, only the lighter fractions escape from the upper layers of the distilland, then heavier fractions commence to distil while further fractions remain undistilled in the stagnant lower layers. This condition, naturally, becomes more pronounced when the distilland is in the apparatus in layers of comparatively great depth.

Thermal Hazard. Thermal hazard results from the fact that, although evaporation takes place from the upper layers only, the whole of the distilland must be heated through the degassing and distillation period, amounting in some instances to several hours of exposure to heat. Thermal hazard is also clearly related to the depth of the distilland charge in the still. Since the rate of evaporation from the surface layers drops when the lighter fractions have been removed, the time taken to distil unit quantity of the material increases as distillation proceeds, so that large charges of distilland need disproportionately long heating periods.

Operational Features. The operation of a pot is by its very nature discontinuous. For example, it is normally necessary to take off the condenser before degassing. It follows that, after degassing, the system has to be rapidly let up to atmospheric pressure, the condenser has to be re-inserted and the assembly pumped down again before the distillation

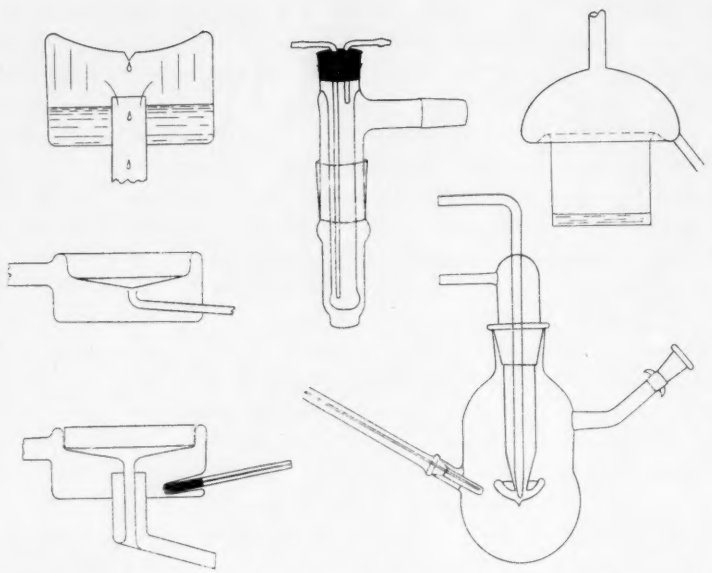


Fig. 2. A selection of pot stills indicating the large variety of forms described in the literature.

can begin. If the condenser were not removed, it would be contaminated by the froth evolved from the charge during the degassing process. Movable condensers have been suggested[18], from which splashed material may reflux into the boiler during the degassing operation, but the drainage of distilland oil from a condenser takes a long time to complete and this affects the composition of the fraction collected, particularly if the charge is small.

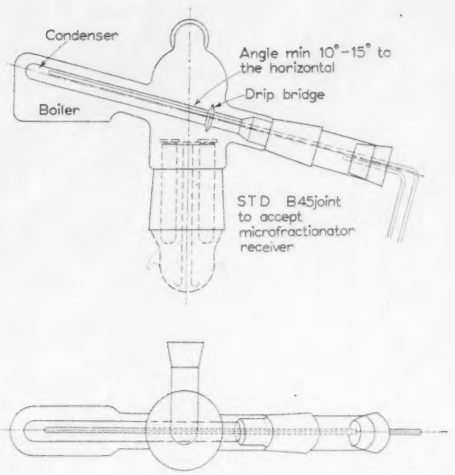
As will have been noticed, the disadvantages of the pot still are of a nature which prohibit scaling up of its dimensions in order to handle large quantities of material. However it still continues to be useful for small amounts of distilland ranging from 0.1 g. to 10 g. where the effects of its disadvantages are minimised, or for rather larger quantities of comparatively volatile or heat-stable distillands, such as the petroleum fractions investigated by Burch[1].

Designs for Fractionating Work

Although pot stills, for preparative work, ceased to be of much commercial interest after the early 1930's, quite a number of laboratory models have been made since, differing in a number of design details. These include the use of standard taper ground glass joints[18], internally positioned electric heaters for the distilland[19], and a heating bath in which a small still can be immersed completely, in order to ensure that all distillate collects on the condenser proper instead of on relatively cool parts of the pot wall.[20]

Babcock[21] made an extremely simple micro-diffusion still from a small test tube with receiver bulbs blown into the tube wall at different heights. By cooling the part of the tube above each receiver bulb separately and in turn, he was able to collect fractions which could subsequently be withdrawn from the bulbs with a capillary pipette. The distilland sample was about 100-200 mg., and was heated by placing the bottom of the tube in an oil bath.

Meunier and Raoul. A modified type of pot still was described by Meunier and Raoul[22] in 1944 and has



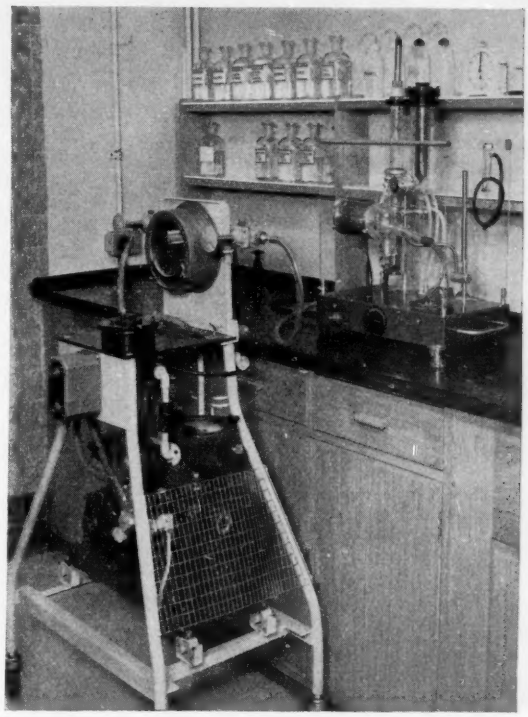


Fig. 3. All-glass semi-micro molecular still based on the Gilson-type of design, suitable for charges ranging from 0.2–5.0 g. The photograph shows the still set up for operation, using a built-in 1-inch diffusion pump. The fore vacuum is provided from the trolley-mounted mechanical pump in the foreground. (*Vitamins Ltd.*)

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been further developed by Gould, Holzman and Niemann[23], Smith and Matalon[24], and Gilson[25] (Fig. 3). This design, by using a horizontal boiler (similar to the Burch[11] tray still) gives a larger effective distilling surface than do most of the earlier vertical models, and is equipped with means for the removal of several fractions without breaking the vacuum. The version reported by Gilson has been commercially available in this country for about six years, and, is one of the very few molecular stills offered for sale by a British manufacturer. In this version a shallow layer of distilland is heated in a horizontal glass tube, about 3 inch. diameter by 10 inch. long, by means of an open-wound Nichrome resistance heater through which the contents of the still can be observed. The distillate collects on a slightly inclined cold finger inside the heated tube, runs along to a projection and drips off into a pig fraction collector. The evaporator-condenser gap is about 2 cm., and it is claimed that samples up to 100 g. can be fractionated, although, when using especially thermo-labile materials, it would probably be advisable to keep the charge down to a minimum.

Gould et al. The still developed by Gould *et al.* is essentially similar to Gilson's model, but is scaled down to handle micro-quantities of material. The size of the charge is about 50–150 mg. and four small glass receivers on a rotating joint are designed to hold about 30 mg. of distillate each. A length of fine glass capillary stands loosely in each receiver serving to lead the distillate down from the condenser projection avoiding dropwise transfer and thus minimising hold-up of the distillate. As the joint is rotated, each of the capillaries in turn is brought under the condenser projection.

Gilson also describes a semi-micro fractionating still in which distillate from a small pot evaporator

collects as a viscous-liquid or frozen-solid layer on part of a cooled glass condenser which may be moved by a magnetic drive operated externally to expose a fresh portion of its surface for each fraction. After distillation is completed, the condenser is removed and the fractions are scraped off separately or taken

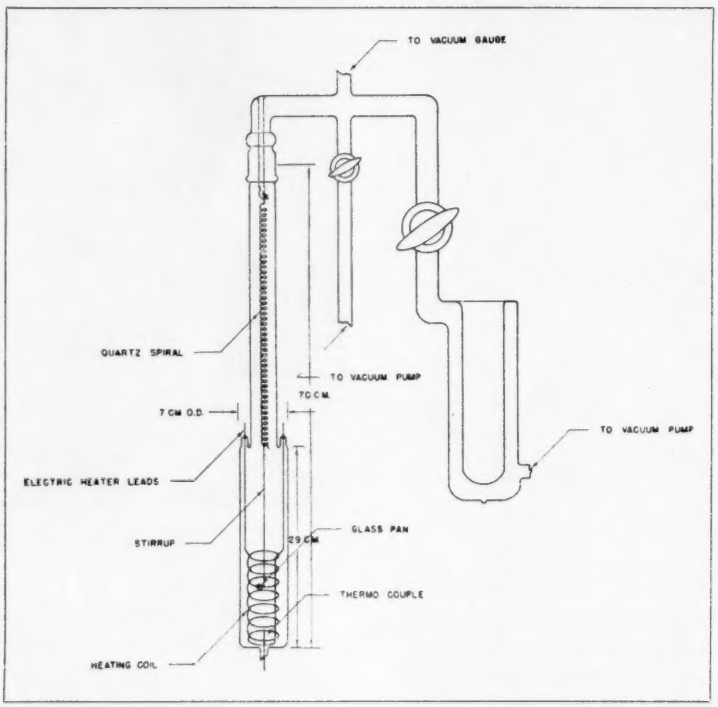

Fig. 4. Diagrammatic view of the Sims still.

up in an appropriate solvent.

A Non-Fractionating Still. A non-fractionating still for quantities of approximately 1 g. was reported as late as 1953 by Meek[26], who claimed that the distillation rates at a given boiler temperature could be raised by increasing the difference between boiler and condenser temperature, and consequently proceeded to use liquid air in the cold finger. As we have seen, under ideal conditions the absolute rate of evaporation is a function of the absolute temperature of the evaporator. The condenser temperature should not, therefore, affect the distillation rate in any way as long as it is sufficiently low to prevent appreciable re-evaporation of the condensed distillate. Indeed, it is probable that the high rates reported were due to the very large condensable vapour 'pumping' capacity of the liquid-air cooled condenser, which would 'clean' the pot still interior down to much lower values of the residual gas pressure than could be reached in a reasonable time by the proper pumps connected to the apparatus *via* a small side-arm, fitted with a stopcock.

Typical Uses of the Stills. The many uses to which pot stills have been put include the larger part of the original investigation work on the distillation characteristics of fat-soluble vitamins A, D and E, of marine oils and fatty acids,[27] and of vegetable oils, all of which are now distilled commercially in large quantities. In the laboratory, pot distillation has been used by Allen[28] to separate progesterone, by Selker and Kemp[29] to purify organic sulphur

derivatives, by Quaife and Harris[30] as an intermediate step in the assay of tocopherols*, and by many others as a generally useful method for the collection of small pure fractions from vaporisable mixtures.

Designs for Analytical Work

Occasionally, pot stills have been used for purely analytical work in order to obtain comparative data on the volatilities of different mixtures. In such work, all that is needed is to weigh out a small amount of the test material, expose it at a standardised temperature and pressure for a given time, then re-weigh the material and thus determine the percentage distilled. Normal pot stills have often been used for the purpose, but as it is not necessary to collect the distilled fraction, no elaborate condenser is wanted and the whole determination can be carried out in simple apparatus requiring but a small sample.

Booy and Waterman[32] described in 1949 a micro-still, designed specifically for analytical work, where the sample was distilled from a plate suspended from a helical spring in a small vacuum chamber. An infra-red lamp was employed to heat the sample. The changes in weight occurring during the distillation were indicated by a corresponding movement of the helical spring, so that a continuous weight measurement was possible.

Sims[33] later modified this apparatus by incorporating a thermocouple temperature indicator and a built-in heating element. In addition, he arranged for a larger distance between the evaporating and condensing sections in order to avoid condensation of distillate on the helical quartz suspension. The Sims still, illustrated in Fig. 4, would take a 30 mg. sample of distilland oil and changes in weight of the order of 0.005 mg. could be detected by measuring the pan height with a cathetometer. Similar apparatus has been described by Madorsky[34] and Jellinek.[35]

Rushman and Simpson. Where relatively large samples are to be tested, the residue may be removed completely from the still and weighed on a balance. Rushman and Simpson[36] describe a semi-micro analytical still consisting basically of a small temperature controlled hotplate in a vacuum chamber. The sample is weighed into a flat metal dish and heated on the hotplate in a high vacuum for a given time. It is then removed, cooled down and weighed again. This apparatus has been used to determine the relative amounts of triglycerides and polymers in linseed oil, and appears to be quite a robust piece of equipment for applications where the elegant continuous weighing facility mentioned before is not needed.

Typical Uses of the Stills. Measurements of the progressive loss in weight of the sample under standard conditions as facilitated by the Booy and Waterman still or the Sims still, are useful in determining, for instance, the degree of polymerisation obtained in a monomer-polymer mixture, as the relatively low molecular weight monomer will distil preferentially. Correction for the volatility of the polymer can generally be made by running synthetic mixtures of pure monomer and polymer at known concentrations and calibrating the still accordingly. Sims discusses the theory of analytical distillation in some detail and shows that, for compounds in the same general chemical class, the molecular weight is linearly related to the median temperature of the elimination curve, *i.e.* the point at which 50% of the material has distilled in a stepwise distillation at progressively increased temperatures.

FALLING-FILM STILLS

Working Principle and General Characteristics

Falling-film stills represented an important advance over pot stills. Here, evaporation was allowed to take place from a thin film of distilland flowing under gravity over a heated evaporator surface, usually shaped in the form of a vertically positioned cylinder. The bulk of distilland was stored at a relatively low temperature and the hot residue leaving the evaporator was passed through a cooler, so that the total heating time of any part of the distilland was reduced to approximately one quarter-minute

* In connection with the assay of tocopherols, it would appear worth mentioning that the paper chromatographic methods developed in the laboratories of the author,[31] have now made it possible to determine individual tocopherols accurately and speedily, even in very low-potency samples, without recourse to molecular distillation or hydrogenation.

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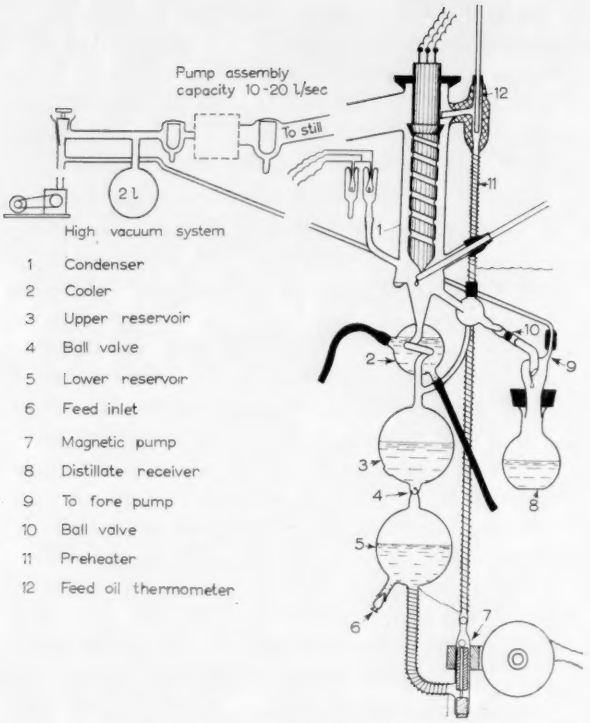

Fig. 5. Hickman's cyclic falling-film still.

during which it flowed over the evaporator.

Fractionation Efficiency. As the distilling film was only about 0.25 mm. thick and slightly turbulent on account of its movement over the evaporator surface, the components of the distilland could escape at more nearly equilibrium rates than in the pot still and hence there was a considerable increase of fractionating capacity. However, there was no reflux washing of the distilling vapours, as in a packed column, and thus, the fractionating power of the falling-film still remained much lower than that of a conventional atmospheric-pressure still.

Mode of Operation. Commercial falling-film still operation generally involved multiple distillation, the distilland being allowed to pass continuously over a series of evaporators at successively higher temperatures until sufficient material had distilled. The distilled fractions were often re-processed in the same way until a high-potency distillate was eventually obtained. Alternatively, a batch quantity of distilland could be re-circulated over a single evaporator, a fraction being collected and the temperature being raised after completion of each cycle.

Early History. The first models were constructed around 1933 by Waterman and Oosterhof,[37] and Carr and Jewell,[38] and were soon improved by other workers. Since the immediate limitations of the pot still had been removed, it became possible to scale up the equipment to sizes capable of handling commercial quantities of distilland.

Patents for falling-film stills were taken by Burch and Bancroft,[39] Carr and Jewell, Fawcett and Burrows,[40] and, notably, by Hickman,[41–44] to whom must go the credit for most of the subsequent development of the molecular distillation industry.

Hickman's Basic Design of the Cyclic Falling-Film Still

Hickman[45], see Fig. 5, described in 1937 a laboratory-size still operating on the principle of re-circulating a batch quantity of distilland over a single evaporator. The design, although old, has served as the basis for many subsequent still designs and therefore merits a short description here.

The evaporator consists of a vertical column, about $1\frac{1}{2}$ inch. in diameter and some 9 inch. long, closed at its lower end and provided with an internal electric heater. The evaporator is mounted concentrically inside a glass tube, about $2\frac{1}{2}$ inch. in diameter, which acts as the condenser and is fitted with a distillate take-off system. Underneath the evaporator section a cooling coil and two reservoirs are disposed, one above the other.

In operation, distilland is admitted to the lower reservoir under rough vacuum and is circulated over the evaporator column by means of a small reciprocating pump. Falling from the pointed lower end of the column, the distilland passes through the cooler and collects in the upper reservoir, while some dissolved gases and volatiles are removed by

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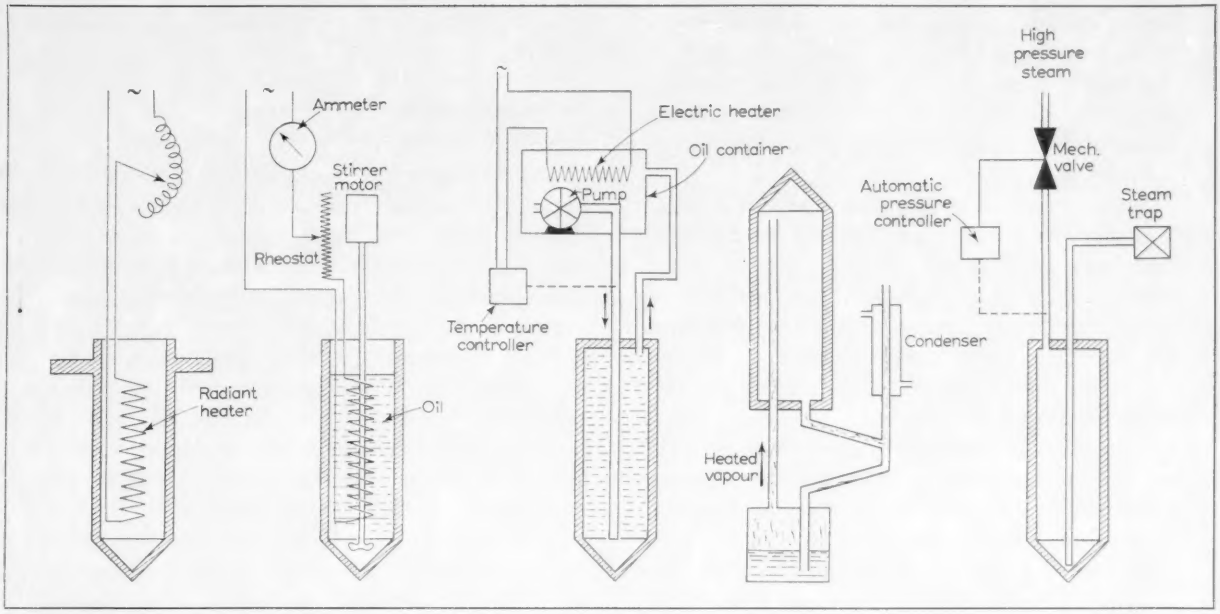
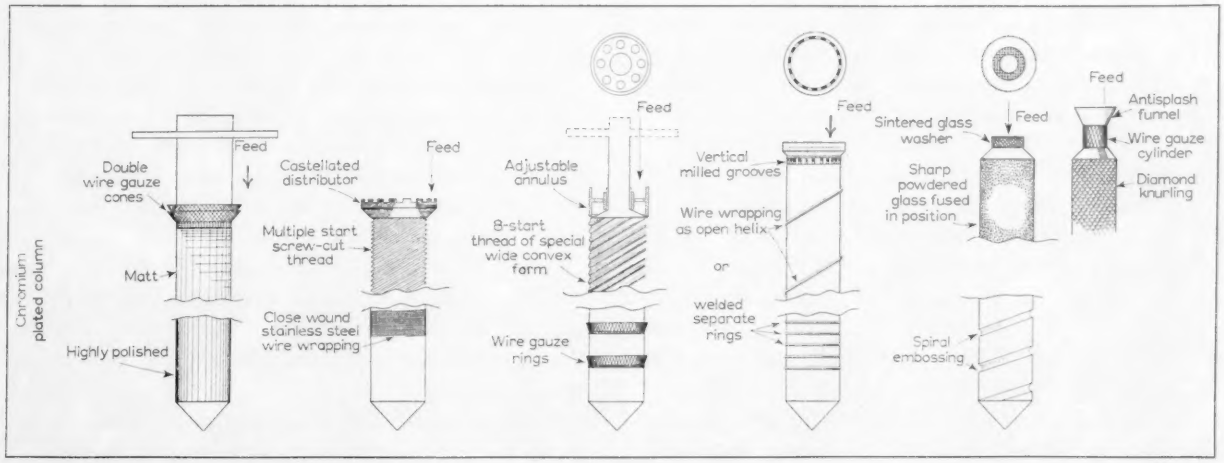


Fig. 6(*a*). (Above). Various arrangements for heating falling-film evaporators: (1) Variac-controlled radiant heaters; (2) oil immersed resistance heater, for greater uniformity of column temperature; (3) hot-fluid circulating system with external thermostatically controlled reservoir; (4) vapour heating system operating at a fixed known temperature and (5) pressurised vapour system giving a wide range of controllable temperatures.

Fig. 6(*b*). (Below). Various arrangements for distributing distilland over the evaporator surface.

Fig. 6(*c*). (Bottom). Various column surfaces. The plain cylindrical surface in matt or polished chromium is suitable for distillands which spread easily. The other surfaces have been used to overcome channelling and poor film formation in distillands spreading with difficulty.



the pumps. The valve between the two reservoirs is then opened, allowing the distilland to flow into the lower reservoir again. The whole cycle is repeated, the evaporator being gradually warmed until sufficient volatiles have been removed and the Pirani gauge indicates a pressure in the micron Hg range.

Subsequently the evaporator temperature is raised until distillation takes place, and fractions are taken after each cycle of the charge is completed or, alternatively, at other times as desired.

The liquid-flow control valves consist of steel balls, seated in ground sockets and manipulated from outside the apparatus by means of an electromagnet. High-vacuum in the equipment is maintained by a system comprising a diffusion pump of about 20 l./sec. capacity backed by a rotary mechanical pump, and fitted with carbon dioxide traps in the high vacuum manifold and backing line. Total vapour pressures are indicated continuously on the Pirani gauge mentioned before and situated near the evaporator.

As Hickman indicated in his original publication, the most critical part of such a still is the distilling column. The distilland must spread evenly without streaming or channelling, otherwise fractionation is spoilt as a result of temperature variations across the surface of the distilland film. In Hickman's own still, even distribution of the distilland is effected by two metal gauze collars of different mesh, wired round the column, just above the effective distilling area. The column itself is made from a copper cylinder and has a polished chromium finish. It is either left plain, or is spirally embossed for all those applications where the distillands spread with difficulty. Various evaporator and distilland distribution systems are shown in Fig. 6 (a-c).

Modifications by Other Workers. Other arrangements have been used successfully. For example, Jewell, Mead and Phipps[46] employed a serrated distributor round the top of the column and wrapped a wire spiral on the evaporator surface. Fawcett and Burrows[40] used rings of wire gauze at intervals, and Detwiler[47] employed a mushroom-head distributor feeding a glass column, on the surface of which a layer of broken glass particles had been fused in order to induce maximum turbulence in the moving oil film.

Still Performance Assessment I. The Elimination Curve

The development of laboratory-size cyclic falling-film stills, substantially similar to Hickman's model, made it possible to investigate the distillation of mixtures with much less risk of thermal decomposition than had been associated with the simple pot still.

We have already seen that compounds cannot be characterised by a boiling-point under molecular distillation conditions. However, the temperature of the elimination maximum of the compound may serve as a property analogous to a boiling-point.

In order to obtain the elimination curve of a compound, it is necessary to distil it under standard conditions from a relatively non-volatile solvent, exposing the compound for a number of distillation cycles at constant feed rate and progressively increasing temperatures, see Fig. 7 (a-e). A fraction is collected after each cycle, allowing a standard time for drainage, and the weight of the compound in each fraction is determined. The successive weights are converted to percentages of the total amount of compound in the distilland. Plotting the %-yields against distilling temperature then gives the elimination curve, its form being more or less independent of the nature of the material distilled.

Variations from the theoretical form are usually indicative of drainage errors, unduly high distillation rates, poor equilibrium, affinity of solvent for the test materials, and non-ideal conditions in general. On the other hand, where the test 'compound' is in reality a mixture of related compounds not distinguishable by normal assay procedure, the plot of the elimination curve may show several maxima. Such multiple curves gave important clues to the compound character of naturally-occurring vitamins A and D.[48]

'Constant Yield' Solvents. In practice, it is not possible to use a completely non-volatile solvent for the compound under investigation but satis-

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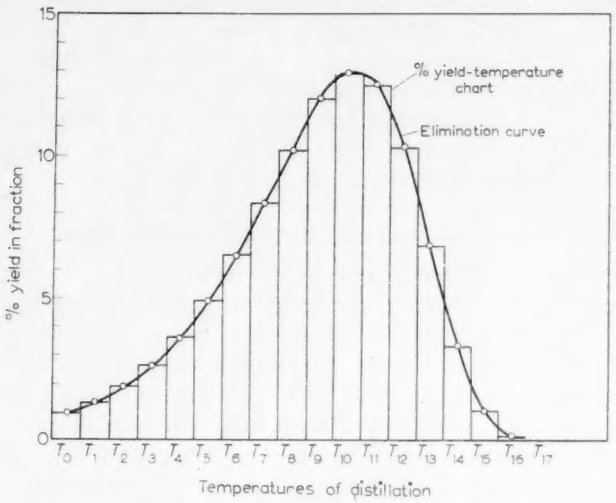


Fig. 7(*a*) (Above). Theoretical elimination curve of volatile material from non-voltaile substrate.

Fig. 7. A selection of elimination curves, both theoretical and practical.

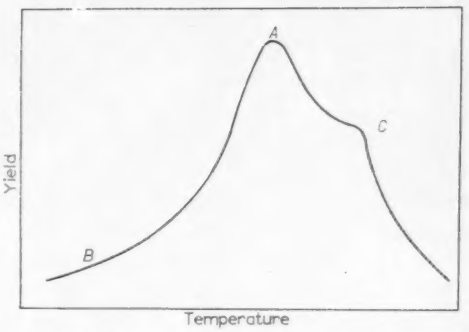


Fig. 7(*b*) (Above). Theoretical elimination curve for 2 volatile components, showing distinct maxima.

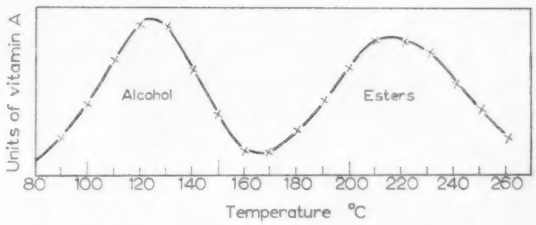


Fig. 7(*c*) (Above). Experimental elimination curve for the distillation of vitamin A from partially saponified cod liver oil. The occurrence of 2 maxima indicates that vitamin A exists in 2 different forms.

Fig. 7(*e*) (Below). Elimination curve of aminoanthraquinone pilot dyes.

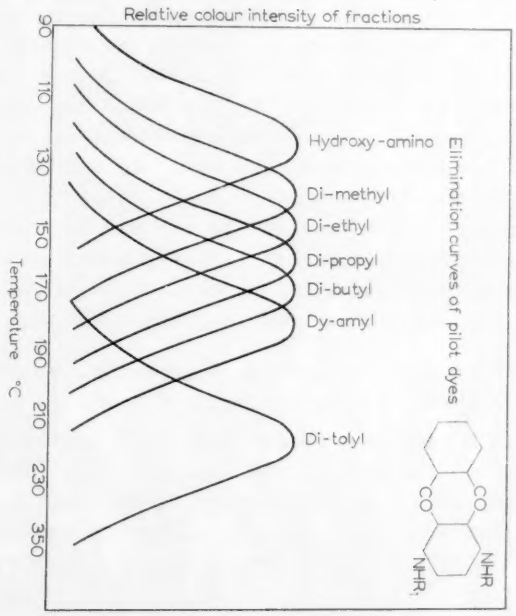
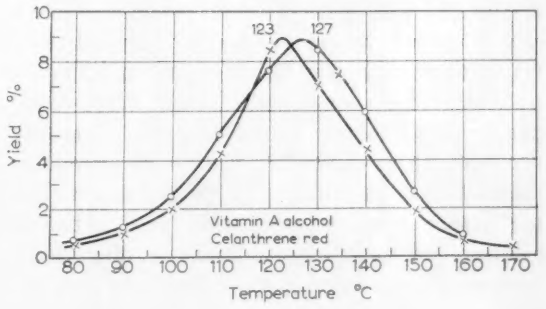


Fig. 7(*d*) (Below). Elimination curves of free vitamin A and of Celanthrene Red.



factory results can be obtained by using a 'constant-yield' oil which gives small fractions of approximately equal weight at each successive temperature level, thus making the drainage error constant for each distillate. Such an oil is usually prepared by blending fractions from the molecular distillation of glyceride or petroleum mixtures. Full details on the preparation are given in the literature.[49, 50]

Dyes for Calibration. Although the exact temperature of the elimination maximum for a given substance may vary slightly from one still to another on account of dimensional differences, the temperature difference between the maxima of any two compounds remains constant. Therefore, once a still has been calibrated in terms of a few well-characterised compounds, the elimination maxima of other known compounds can be predicted for that particular still. Conversely, the elimination maximum of an unknown substance will be a guide to its identity.

Dyes, notably the oil-soluble anthraquinones, are extremely useful for calibration purposes since their concentration is easily determined by colorimetric measurement, and a wide range of temperatures may be covered with different dyes. Although the whole subject of elimination curves and pilot dyes has been dealt with very adequately by Embree[3], it may be worth dwelling in greater detail on one important use for dyes, *i.e.* their application in the concentration of materials, such as vitamins, from natural sources.

In this technique, the elimination curve of the vitamin is determined by distilling a small amount of the pure material from a constant-yield oil. A marker dye is then selected, the elimination maximum of which coincides as nearly as possible with that of the vitamin (*e.g.* Celanthrene Red 3B would be used as a pilot for Vitamin A), and a little of the dye is added to the natural oil from which the vitamin is to be distilled. Then, in all subsequent distillations or re-distillations, we can assume that the vitamin distils together with the dye, and in assessing the operating conditions for the regular process of concentrating the vitamin, we may use the colour of the distillates and residue as a simple, rapid guide to the performance of the still in question, instead of having to carry out the rather elaborate assay procedures necessary to estimate the vitamin itself. The regular process can then be carried out without the pilot dye, by applying the same conditions as those known from the initial run to lead to the highest concentration of the dye.

General Scope of the Falling-Film Still

Methods such as these enabled the Kodak team, now operating under the name of Distillation Products Industries (D.P.I.), to develop commercial methods for the preparation of vitamins, sterol acetates, glycerides, low vapour-pressure pump oils, etc., using large equipment. Between 1939 and 1941, in the heyday of the commercial falling-film still, models were constructed with capacities of up to 8 tons per day.[47]

Eventually, as with pot stills, a practical size limit was reached when further increases in evaporator height would have resulted in dangerously long exposure times for the more thermo-labile distillands, such as vitamin oils.

By the end of 1941, all the D.P.I. falling-film stills had been replaced by rotating-evaporator models where centrifugal force was used instead of gravity to produce a very thin, rapidly moving distilling film. Nevertheless, the falling-film still has continued to be of interest in the laboratory, on account of its relative simplicity and low cost coupled with good performance in the small-size range. Commercially, it has been used by countries less technologically advanced than the United States, where the construction of the complex centrifugal stills would have presented major engineering difficulties.

Design and Performance Features of Principal Stills for General Use

The variety of problems involved in the construction of molecular stills, even on a laboratory scale, has caused many workers to build simplified or perhaps over-simplified equipment, omitting some or all of the refinements of the American prototypes.

Farmer and Sutton Simplified Still. Farmer and

Sutton[51], for example, described in 1946 an all-glass falling-film still constructed after ten years' research on the subject. The re-cycling facility, the distilland feed pump and the variable evaporator temperature control, had all been omitted in the interest of simplicity. The authors did not elaborate on the specific uses of this skeleton still, but remarked, in their report, on the almost complete absence of reliable information covering details of falling-film still construction, at that time.

In the view of the author of this paper, Hickman's Notes[45] on Apparatus and Methods published in 1937, are a mine of practical information, and for the reasons stated below he would prefer to see the facilities omitted by Farmer and Sutton retained, at the risk of making the construction a little more complex. Going over the points, one by one, the following considerations would seem to apply.

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Re-cycling is not only essential, if elimination curves are to be plotted, but is very useful for the degassing operation. Liquids vary considerably in their behaviour during degassing[2] and may need a larger or smaller number of degassing cycles to reach a state suitable for distillation. If one liquid is to be compared with another by distillation under similar conditions, it should be possible to give each material individual degassing treatment beforehand. With the simplified equipment, the distilland passes continuously through a degassing vessel at 0.1 mm. Hg. pressure and thence over the evaporator, so that both operations are carried out at the same rate whatever the nature of the distilland.

The feed pump is important as a precise controller of the feed rate. Needle valves, however carefully made, allow the rate to vary according to the hydrostatic head, viscosity, density, etc. of the distilland, whereas a positive displacement pump gives a predetermined rate and maintains it throughout a distillation run, more or less independently of the head of oil in the reservoir. During a molecular distillation process, moreover, it is the time-temperature relationship which governs the amount of distillation. Both parameters, therefore, should be accurately controllable.

Finally, a word on variable evaporator temperature control. The simplified model maintains a reproducible temperature by means of a solvent reflux system operated by an electric heater in the evaporator column. It is, however, relatively easy to provide satisfactory means for the variation of temperature either in the form of a simple energy regulator or of a thermostatically controlled heater, and the convenience of being able to select temperatures for fractions is well worth some elaboration.

Taylor's All-Glass Still. As an interesting comparison, we may note Taylor's simple all-glass still[52] built in the same year, which retains all the functions of Hickman's model but has a reduced dead-space so that charges down to 10 ml. may be handled. The feed is pumped through an annular orifice at the top of the evaporator column as is the case in Detwiler's still.

The existence of a dead-space between the feed pump and the evaporator oil spreader is the one minor drawback of pumped stills. Reducing the cross-section of the feed pipe causes excessive viscous drag with some oils, and normally a 2-3 mm. bore seems to represent the practical minimum.

Breger's Double-Ended Still. An ingenious solution to the problem of handling semi-micro quantities of feed oil is to be found in the Breger double-ended still,[53] designed for handling 1-5 g quantities, see Fig. 8. This is a vertical column still with two similar ends, each having oil storage and distillate removal facilities. The distilland is allowed to run from the upper receiver, through a glass stopcock giving a rough measure of rate control, over the evaporating surface and thence into the lower receiver. After the distillate has been drained and collected, the whole still is inverted and the process is repeated at the temperature required for the next fraction. Breger's evaporator consists of a length of 28 mm. diameter glass tubing, with a spiral of 1 mm. platinum wire wound at a 15° pitch on its inner surface. The distilland runs down the inside of the tube and is spread evenly across it by the wire spiral. Heat is supplied to the outside of the tube from a resistance coil situated in a glass jacket surrounding the distilling area, and the distillate collects on a glass

condenser made from 3 mm. tubing, positioned concentrically to the evaporator and projecting through the ends of the still. Distillate receivers are connected to this still through two-way stopcocks, so that fractions may be removed and clean flasks

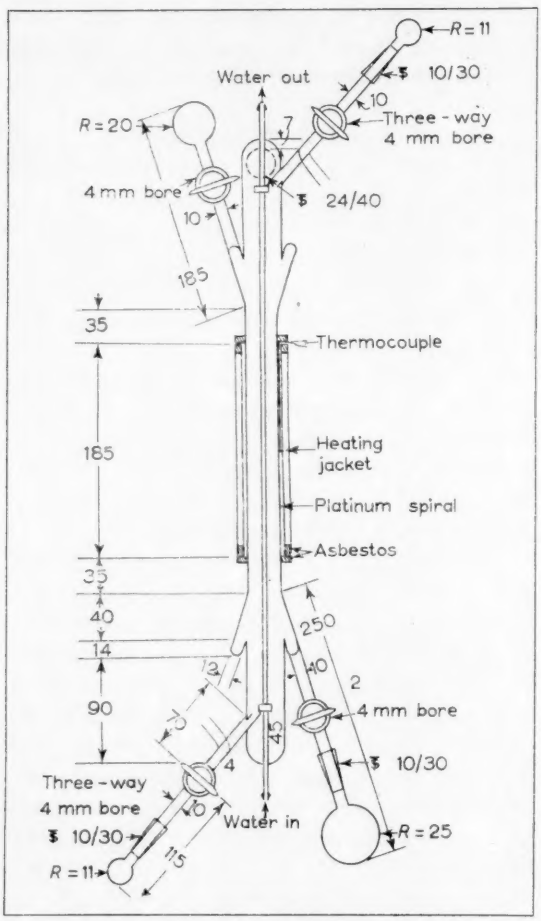

Fig. 8. Breger's semi-micro molecular still.

attached without breaking the high vacuum in the main part of the still.

Apart from the possible risk of breaking the still whilst inverting it, the operation of the apparatus seems attractively simple. However, it requires about half an hour for the fractions to drain through the collection system and stopcock, if a complete recovery of each distillate is desired.

Variations of the Breger Still. In 1949, Roper[54] described a still, similar in principle to Breger's but capable of handling viscous distillands that would not pass readily through small stopcocks. The evaporator, unlike Breger's, operates at about 30° to the horizontal. It is made of 26 mm. Pyrex tubing, 380 mm. long; the ends are sealed and slightly bent downwards to form reservoirs.

When the still is carefully tilted about the central vacuum connection, distilland overflows from the upper reservoir and runs down the lower inside surface of the evaporator tube to the reservoir at the bottom. The central portion is electrically heated, and the fractions collect on a concentric glass condenser as in the Breger still. After removal of the fraction, the still is tilted in the other direction for the next cut to be taken. The Roper still has been used to fractionate a 14.5 g. sample into seven 2 g. cuts, and is obviously of a convenient size for the laboratory.

However, one would expect it to be difficult to control the distilland accurately by tilting the apparatus, and hence, it must be difficult to reproduce operating conditions. Most probably, therefore, such equipment is mainly useful for the separation of a fairly volatile distillate from a very much less volatile residue, a type of process, where variations in rate, thickness and exposure time make little difference to the eventual composition of the fraction. Another variation of the Breger still was developed in 1954 by Inoue[55], who used the apparatus for the very process just mentioned in order to purify organic compounds.

If an analytical distillation is required to be carried out on very small quantities under reproducible conditions, the most reliable method is probably that of diluting the sample with a suitable grade of constant-yield oil and then distilling it in a cyclic falling-film still, making certain that all operating conditions are closely controlled. A minimum volume of about 25 ml. is necessary, for a carefully constructed still following Hickman's pattern.

Santiago and Gonzalez-Montes Still. A hint as to the general usefulness of the cyclic still is given in a

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paper by Santiago and Gonzalez-Montes[56], who, having bought a ready-made falling-film still from Schott and Genossen of Jena, found it worth modifying the whole apparatus to bring it in line with the familiar Hickman design. The oil distribution system gave some trouble, however, and eventually a new arrangement was adopted. In this, a stainless steel gutter, into which the oil is fed, surrounds the upper part of the evaporator. Oil escapes through a large number of vertical grooves between the gutter and evaporator and flows down evenly, spreading being further assisted by a closely wound spiral of stainless steel wire enveloping the whole of the evaporator surface.

Unsupported Falling-Film Stills. Another unusual solution is contained in the proposal[83], see Fig. 9, aiming at removing wholesale all difficulties experienced in forming a film without channelling, overheating, or the gradual build up of a polymerised layer. In this system the solid column is eliminated altogether, and the oil falls as a film or sheet supported only by two guide rods on either edge. The oil is preheated just before flowing down through a large number of holes to form the continuous free film, and distils in the usual way on to one or more condensers. Incidentally, the idea of using an unsupported film or sheet was given a practical test by Hickman[84] some years earlier when he recirculated a proportion of his distillate through an external cooler, spun the cold distillate into a flat disc by centrifugal force, and used the resulting cooled disc as a condenser of low thermal capacity.

Both these ingenious ideas, however, seem to have lapsed into obscurity, as far as the general literature indicates.

Stills for the Study of Tocopherols

Various cyclic falling-film stills have been built in the laboratories of the author, largely for the study of tocopherols.

Initially, the work was carried out in a still which was a fair copy of Hickman's design, but the team's knowledge of American procedure was somewhat incomplete at that time and based on current publications, patents etc., giving limited information only. Thus it happened that a published account of the early phases of that work dealing with the practical conditions governing the concentration of tocopherols from natural sources, recorded the opinion then held by the Vitamins group of workers, that the American method required a chemical concentration procedure to be applied either before or after the molecular distillation process, in order to obtain high potency concentrates (say 50%) of tocopherols. These statements were corrected by

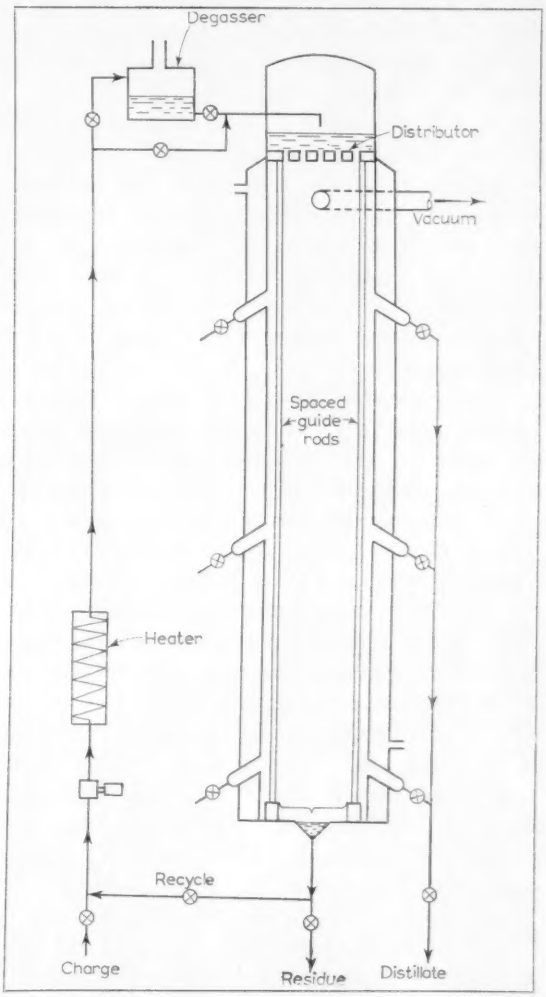


Fig. 9. Ferris' guided free-film still.

Hickman in his annual review of 1951[58] and today it is a well-known fact that in that year the U.S.A. had already large multiple still assemblies in operation capable of handling hundreds of tons of vegetable oil in counter-current flow, producing final distillates containing between 20% and 50% mixed tocopherols. Also, high-potency distillates were being produced from deodoriser sludge, one of the vegetable oil refinery by-products containing about 3-5% tocopherols.

The lack of comprehensive information on progress made elsewhere resulted in an early decision by the Vitamins team to start their own full-scale investigation into the principles applicable to large-scale commercial processing. Thus, a methodic study was conducted into the effects of varying the pumping rate, the evaporator surface, the type of vegetable oil etc., using both crude and normally refined oils.

Using a column with a distilling area of about 150 cm². and a height of 15 cm., it was found that distillation took place under equilibrium conditions at oil flow values up to about 10 ml./min., but that higher rates gave distorted curves with poor separation of fractions. The apparent maximum of the tocopherol elimination curve was naturally displaced to various positions in each of the oils tested, by the distillation of other materials, including sterols and fatty acids, in varying quantities. Although refined oils did not contain much of these volatile constituents and, moreover, kept the apparatus appreciably cleaner than did crude oils, a large part of their original tocopherol content had been destroyed during refining and consequently they were unsuitable as commercial starting materials. Rather surprisingly, wheat-germ oil, although the richest natural source of tocopherol available in practical quantities, was also unsatisfactory as it degassed only with difficulty, charred on the evaporator and distilled copious amounts of low-temperature fractions which appeared to swamp the evaporator-condenser gap and made it necessary to run at reduced rates. Cottonseed and soyabean oil, on the other hand, both distilled well. A typical set of distillation results is shown in Table I.

Table 1. **Distillation of Refined Soyabean Oil (138 g.) Distilland Pumping Speed 6.5 mls./min.**

Temp. of Fraction °C	*Wt. of Fraction g.*	*Toco-pherols mg/g.*	*Total Toco-pherols g.*	*Distillate Combined Potency mg./g.*
150	0.48	7.4	3.5	7.4
160	0.51	7.1	3.6	7.2
170	0.34	21.9	7.45	11.0
180	0.43	42.3	18.2	18.6
190	0.43	68.0	29.3	28.4
200	0.96	35.8	34.4	30.6
210	2.00	3.48	6.95	20.1
220	3.75	2.00	7.50	12.5
Original Oil	138.0	0.85	117.0	—

Apparent input mixed tocopherols,	mg.	— 117.0
Apparent output in distillates,	mg.	— 110.9
Recovery,	%	— 95
Total amount of material distilled,	g.	— 8.9

At a later stage of the work, when the team was more fully experienced with regard to the operating characteristics of the Hickman still, it became desirable to make certain design modifications. These applied, in particular, to the circulating pump the evaporator assembly and the heating system. Fig. 10 (a-b), gives details of the final construction of the still as employed in the work described.

The original circulating pump gave trouble. As mentioned above, some distillands degassed only with difficulty and continued to evolve bubbles while being recycled over the evaporator during the degassing period. Often bubbles appeared in the circulating pump as the plunger fell, and eventually a gas space would develop between the plunger and the ball-valve. At this stage, with a bad distilland, the pump might cease pumping oil, and merely compressed and released the gas in the space at each stroke. The difficulty was overcome by making up a small gear pump to replace the original reciprocating type. The gears were ten-toothed spur gears, about 3/16 inch, deep by ½ inch pitch made of chromium-plated mild steel, and displaced about 0.2 ml. per revolution. The pump body was machined from a short piece of hard-drawn aluminium rod. 'O'-ring seals were used to ensure vacuum-tight mounting of the end cover, drive

shaft and oil pipes. This arrangement worked very satisfactorily, giving an even flow of oil. It was hoped that the risk of metallic contamination would not be any more serious than with the reciprocating pump, and up to now no such troubles have been encountered.

A novel stainless steel distributor in the form of an adjustable annulus has been fitted to the evaporator. The two components of the distributor are threaded together so that they may be opened up for cleaning and then re-set readily to the required gap. It has been found that the double wire gauze collar, originally present, would promote the formation of asymmetrical deposits of polymerised oils or carbonised gums and thus spoil the distribution, when crude distillands were processed. Cleaning out these deposits was no easy matter, whereas the hard steel edges forming the annulus could easily be separated and scraped if necessary.

The evaporator itself is made from hard brass, 1-1/8 inch diameter by 5 inch. high., nickel-plated and dull chromed. On its surface is an 8-start thread with a 30° pitch. The form of the thread is such that the film is of fairly uniform thickness, while most of the effective distilling surface is convex in two dimensions in order to give a maximum mean free path to the distilling molecules. The column is supported from the stainless steel flange above on a 6 inch. length of 5/8 inch diameter stainless tubing, which on account of its low thermal conductivity transmits very little heat to the Neoprene gasket sealing the flange to the upper part of the glass condenser.

Finally, the column is heated with oil, circulated rapidly through it from an external system with thermostatic control. Simple 'on-off' control with a bimetallic regulator has been quite adequate to ensure a maximum differential of ± 1°C., and this method enables the operator to raise the column quickly to the desired working temperature without trouble. Previously, it was necessary to adjust the heat input with a rheostat or variable transformer to correspond to the rate of oil flow, specific heat, etc., and thus a given control setting did not always produce the required temperature.

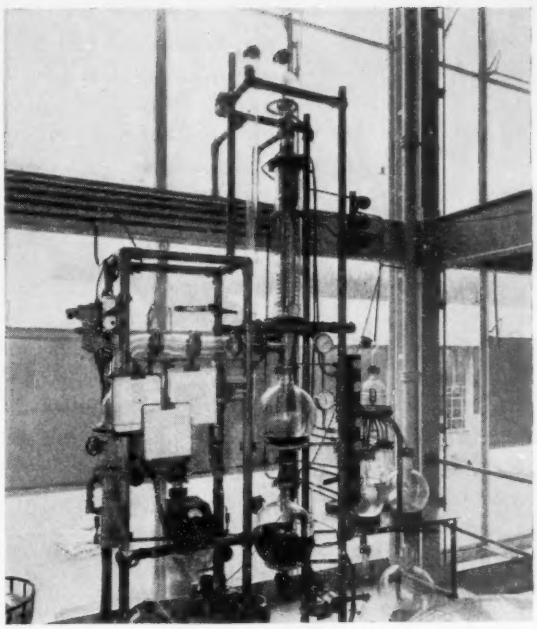
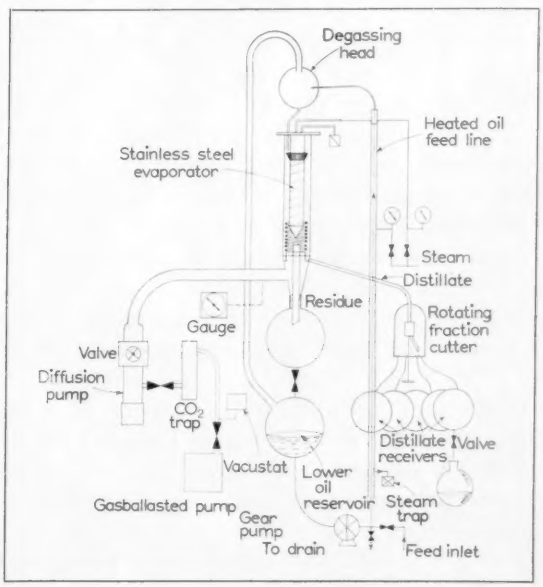


Fig. 10. A pilot-scale falling-film still for charges up to 20 l. The stainless steel evaporator is heated by pressurised steam as shown in Fig. 6(*a*) The feed pump is of the vacuum-sealed type and need not be immersed in oil.



Reports on Russian and Japanese Work

An investigation on the concentration of tocopherols was reported fairly recently from the Soviet Union. Shipalov and Burnasheva[59] distilled cottonseed and soyabean oils on a Russian-built falling-film still, producing curves much like those obtained by the Vitamins team, but the recovery of tocopherols in the distillate was lower, varying from 25-36%.

The oils gave a maximum potency of 4-6% tocopherol in the 170°C. fraction. By re-fractionation this could be concentrated to 6-12% tocopherols, and then by further treatment including neutralising fatty acids and freezing out sterols a final potency of 48% tocopherols was achieved. The original oils were in the range 0.1-0.2% total tocopherols as measured by Quackenbush's[60] variation of the Furter-Meyer method, now superseded by the paper chromatographic assay.[31] The high potency tocopherol concentrates were used at a 3-6% level as antioxidants for Vitamin A preparations, also made by molecular distillation.

Initial work on the Vitamin A process was published by Kogan[61] in 1946, including notes on laboratory experiments with a falling-film still: 92% of Vitamin A was recovered in fractions taken over the 90-260°C. range. Similar work has been conducted in Japan. A falling-film still for production purposes is described by Haychiya[62] in a Japanese patent published in 1954. It is a conventional-type vertical still, the condenser being positioned within the evaporator the outside of which forms the wall of the vacuum chamber. Heating is accomplished by means of a fluid heat-transfer medium passing through a jacket surrounding the chamber.

The oil distributor is interesting, if not entirely novel. It consists of a disc, rotating about a vertical axis concentric with the evaporator, just above the condenser. The distilland is fed on to the centre of the disc and is then flung uniformly outward to the evaporator walls by centrifugal force, while appropriate splash guards prevent distilland reaching the condenser.

Such a rotary distribution system is very effective and not normally subject to unevenness resulting from the carbonisation of material. In the laboratories of the author the principle has been employed for years in degassing equipment, where the oil flows down the inside walls of a heated and pumped vertical tube as a thin film from which the occluded gases and volatiles can escape readily.

Using whale oil as a raw material, Vitamin A yields of up to 135-170% may be obtained, according to Agawa[63] *et al.* These high yields result from the decomposition of Kitol present in whale oils, forming Vitamin A at temperatures around 250°C. Further information on fish-liver oil is given by Suzuki,[64] and analytical distillation work on the composition of some seed oils has been described by a number of Japanese workers.[65–68]

It is understood that falling-film stills are used quite extensively in Japan for the commercial concentration of Vitamin A.

MULTIPLE-EFFECT DISTILLATION UNITS

There have been no significant changes in the pattern of the straight-forward falling-film still for some years now. The main development appears to have been a search for higher fractionating power by the use of multi-stage assemblies. We have noted previously that many of the early commercial installations operated on the multiple distillation principle but with certain exceptions they normally comprised several individual stills. The more recent multiple stills usually constitute a single piece of equipment filled with a plurality of evaporator-condenser units and a common vacuum pumping system. Some of these units are true falling-film stills, but others would be more accurately described as multiple pot-stills through which distilland flows continuously instead of remaining stagnant.

Early Designs

Wollner, Matchett and Levine. One of the earliest multiple stills was constructed by Wollner, Matchett and Levine[69] in 1944. A later version operating on similar principles was employed by Madorsky, Bradt and Strauss[70] in an attempt to fractionate

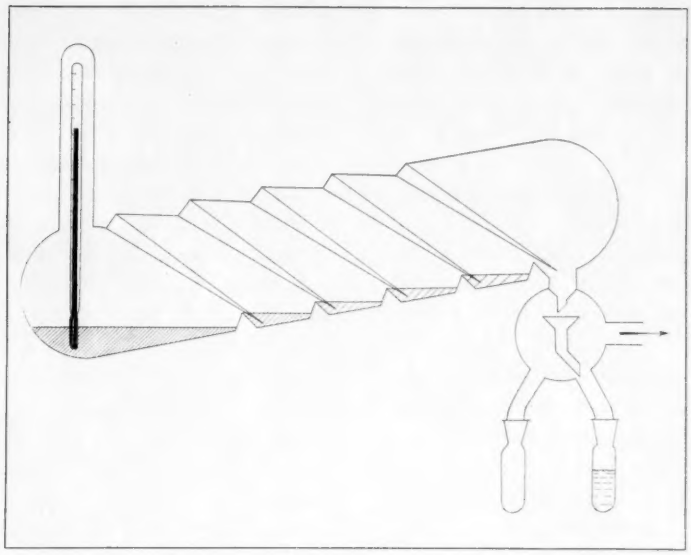


Fig. 11. Diagrammatic view of the Wollner still, facilitating partial counter-current distillation. Heat is supplied along the bottom and condensation takes place in the upper-portion.

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isotopes of mercury. Basically, the latter consisted of a long glass tube inclined at 7.5°-10° to the horizontal, the underside having indentations at intervals which divided it into a series of adjacent cells, each filled with distilland. Above each cell was a sloping condensing surface, arranged to deliver condensate to the next cell above it, see Fig. 11.

In practice, each cell was heated and a small fraction distilled from it into the next cell, while a corresponding amount of heavy residue was displaced down the system towards the lower end. In spite of its ingenuity, the original apparatus gave disappointing results, even though in this particular application there was no risk of thermal hazard so that distillation could safely be prolonged.

The density change under equilibrium conditions was about 1 p.p.m. per cell in the mercury still.

Madorsky. Subsequently, Madorsky[71] built a much more successful multiple-effect still with ten falling-film columns, each one of 300 cm². surrounded by a water-cooled condenser.

The layout provided for the distilled fractions from each column to flow down under gravity over the next lower column for re-distillation, while residues were mechanically pumped in the opposite direction. At 10-20 micron Hg pressure, this arrangement gave an equivalent separation of 13 theoretical plates.

Still Performance Assessment II. The Separation Efficiency

The separation efficiency of molecular stills is generally measured nowadays by distilling a standard binary mixture, such as Octoil/Octoil S (di-(2-ethyl hexyl) phthalate/di-(2-ethyl hexyl) sebacate), see Fig. 12. Paraffin mixtures have been employed for the pur-

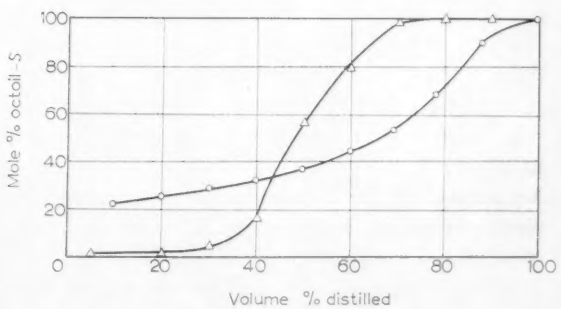


Fig. 12. Molecular distillation of 50 mole % Octoil and Octoil S. O-One-stage molecular still; △-20-stage molecular still. (*Melpolder, Washall and Alexander*).

pose, but generally speaking are less reproducible in quality, whereas Octoil and Octoil S are commercially available as pump fluids and may readily be redistilled to suitable purity, fractions being taken with $N25_D$ 1.4846 and 1.4486, respectively. The mixture has one disadvantage, *i.e.* it does not wet glass under distilling conditions. Consequently measurements on glass columns give poor results.

Torpidity. Hickman and Trevoy[72] carried out various interesting studies on the measurement of evaporation rates from mixtures of di-(2-ethyl hexyl) phthalate (E.H.P.) and di-(2-ethyl hexyl) sebacate (E.H.S.) or of di-*n*-octyl phthalate (N.O.P.) and E.H.S., demonstrating that distillation took place at approximately the theoretical rate calculable from Langmuir's equation, provided the surface was absolutely clean. But the most minute traces of contaminant could form a skin over the distilland surface and depress its distillation rate by a factor of as much as ten. The development of torpidity would be practically inevitable in any liquid surface not constantly renewed by stirring, shearing or overflowing, since 1 contaminating molecule in 10^7 would be sufficient to produce torpidity in one litre of liquid kept in a 2-l. flask.

These results of the investigation into torpidity phenomena almost certainly give the clue to the disappointing performance of Madorsky's first multiple-effect still, which was virtually a series of pot stills in which the liquid moved only very slowly, and the conversely good performance of the second still where surface renewal was efficient. They also furnish an explanation with regard to the malfunction of the Wollner *et al.* still. Although the latter claimed that the distilland surface would be agitated and renewed by the movement of distilland and distillate, the movement was probably inadequate.

Separation Efficiencies Attainable in Practice. In view of what has been said it can be expected that molecular distillation from a pot still without artificial agitation of the surface will give distillation rates well below the theoretical, together with a poorer-than-unit separation. In fact, experiment showed that an unstirred pot still had a separation of only about 1/3 theoretical plates, whereas stirring increased the separation to 1 plate. Lagged pot stills, stirred and working at extremely low distillation rates, managed to achieve separations of up to 2 plates by some degree of reflux washing on the still neck below the condensing zone.

Falling-film stills, where reflux washing is not normally feasible, are limited to a maximum efficiency of 1 plate, but on account of their good surface renewal, they are able to operate right up to this maximum level for distillation rates in the range 2-3/g./sec./m^2., falling off sharply beyond 4 g./sec./m^2. At lower rates, the efficiency drops on account of channelling.

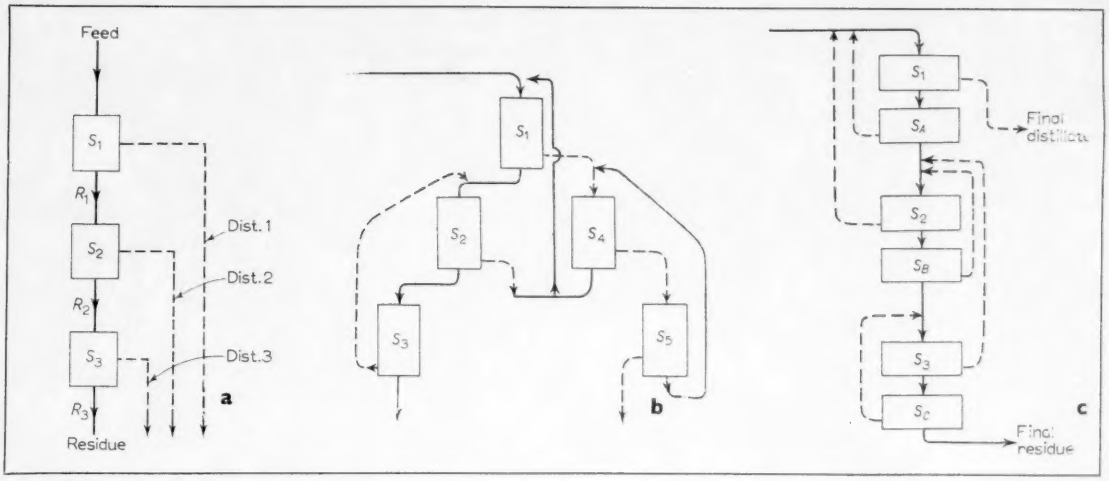
Not more than 5% of distilland should be taken off in one pass if these efficiencies are to be maintained, otherwise the variation in composition of the distilland from the top to the bottom of the column will give rise to a corresponding mixed distillate of poor apparent separation.

The separation efficiency of a multi-effect still attainable in practice depends in part on the particular arrangements made for refluxing both the distillate and the residues, and in part on the arrangements made for taking-off the fractions. Various arrangements have been described by Hickman,[76] Fawcett,[77] Fraser,[78] Booy[73] and others[71,39,42] each suiting a specific purpose, see Fig. 13. In industrial plant, for example, it is usually necessary to withdraw fractions continuously and to restrict the time required for processing the material to a minimum.

In the laboratory, on the other hand, it is often convenient to use batch multi-effect assemblies from which no fractions are withdrawn until all the stages have reached equilibrium with each other.

Still Performance Assessment III. The Thermal Hazard

Thermal Hazard must be considered carefully in each application, and a detailed study of hazard in stills has been published by Hickman and Embree.[79] In order to facilitate comparison of stills in this respect these authors have introduced a number of new expressions and relationships, including



(Above). Flow sheet for fractional distillation according to schemes of Burrows (a), Fawcett (b) and Fraser (c). Distillands and residues are shown as solid lines; distillates as open lines.

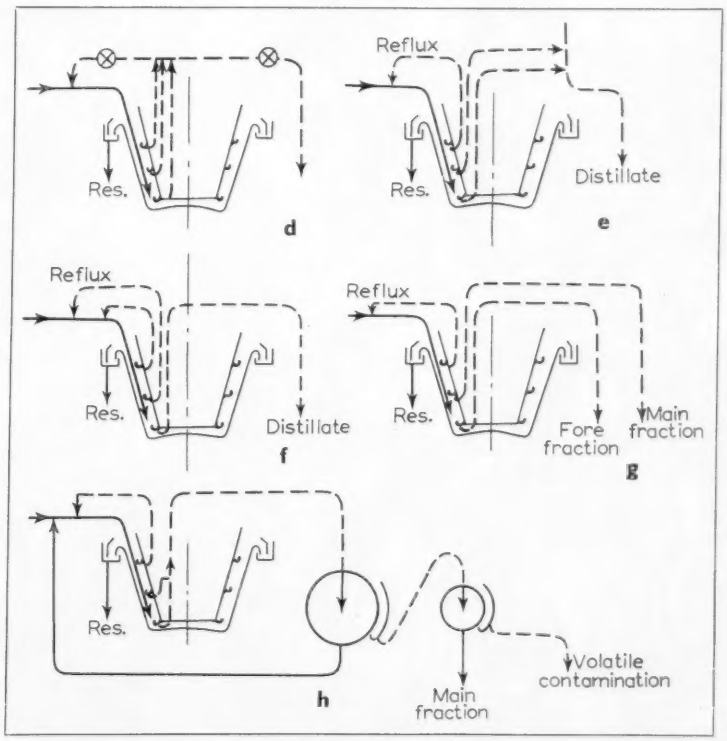


Fig. 13. Various schemes for multiple-redistillation are shown. The choice of methods depends on the relative quantities of final distillate and residue, and on the thermolability of the material processed. For example, 13(a) (g) (h) are all suitable for the removal of low-boiling contaminants.

(On the right). 5 linkages for simple fractionation as used with the 5-ft. centrifugal still.

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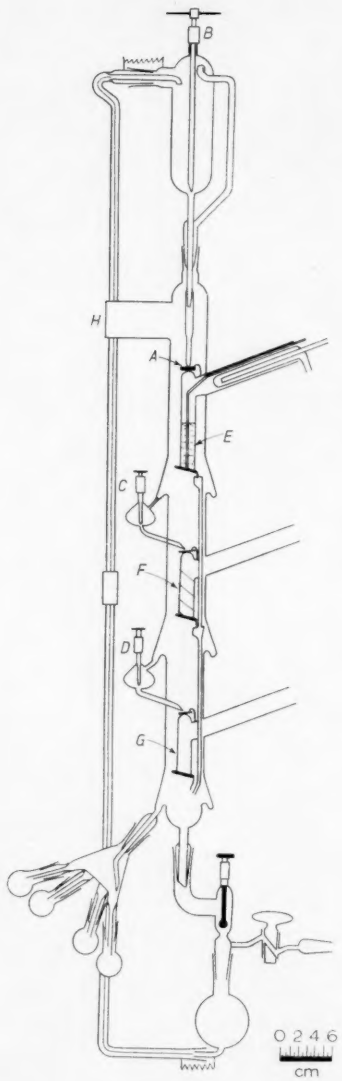

Fig. 14. The Sutton still. *Legend:* A-sintered glass washer; B, C and D—labyrinth screw valves; E, F and G—columns; H—vacuum manifold.

Decomposition Hazard	$D = t_{\text{secs}} \times p_{\text{microns Hg}}$
Hazard Index	$D_h = \log D$
Fractionating Index per Plate	$F_h = D - \log P$

Where P = No. of plates

Most stills have a hazard index ranging from −0.1 to+11.0. A comprehensive table given by Hickman and Embree shows for the

Simple pot still	$D_h = 3.56$ at 1 micron Hg
Wollner's Sloping Multieffect Still	$D_h = 3.86$ at 1 micron Hg
Laboratory Falling-film Still	$D_h = 2.3$ at 1 micron Hg

The latter figure applies under average complete distillation conditions (10 passes).

Corresponding figures are quoted for the maximum permissible D_h level when distilling specific materials: For example

Triglycerides	$D_h = 2.3$
Vitamin-A esters	$D_h = 1\text{-}2$
Activated sterols	$D_h = 0.$

These figures are a useful guide for the determination of appropriate processing conditions.

Multi-effect stills of the cascade fractionator pattern, such as Wollner's and Madorsky's early models, clearly have relatively high D_h values and are unsuitable for such materials as vitamins, sterols, etc. On the other hand they are of great value in the processing of thermostable distillands such as mixtures of paraffins or waxes, particularly where operations are on a laboratory scale, since the fractionating effect of one run to equilibrium conditions may be equivalent to fifty or sixty single-effect passes.

Design and Performance Features of Principal Stills

Booy. There are some minor disadvantages in

Madorsky's ten column still; as a result of the reflux flow arrangement, it is necessary to distil 50% of the feed in each stage, so that a continuous supply of material is available in the end stages with all the evaporators operating simultaneously and at the same rate. Moreover, the pumps and pipelines have a hold-up or dead-space of about 1,200 c.c., so that a rather large sample of distilland must be available. Booy's still[73] has a smaller dead-space and is efficient but rather complex.

Sutton. To overcome these difficulties Sutton[74] has devised a simpler pattern of multiple-effect still in which all columns are not necessarily distilling at the same time. The distillate from each stage runs into a reservoir with a labyrinth screw valve, and from this it may be run over the next lower column at any required feed rate by an adjustment of the valve position. Each reservoir is allowed to fill up before the valve is opened, so that the lower columns operate only intermittently while the top column operates continuously. In this way, the take-off per stage may be limited to well under 5% if necessary and the separation is correspondingly improved. By combining the residues from all stages and returning them to the top reservoir by air pressure, Sutton loses some of the benefits of complete countercurrent operation but, on the other hand, is able to dispense with pumps, cutting his dead-space down to a figure of only about 4-5 ml. Sutton employs three columns, made of glass with sintered glass washers at the top for oil distribution, see Fig. 14. The surfaces are roughened, and have a platinum wire wound on them. Heating is effected, as in the earlier Farmer and Sutton model, by the reflux of boiling solvents in the columns, and, again as before, the screw oil valves require an occasional adjustment to compensate for loss of oil head in the reservoirs. The valves themselves depend for their leak-tightness on having a fine, greased, spindle thread presenting a long gas-leakage path. In the experience of the author, it is quite satisfactory to use a shaft for such duties, made from polished steel and running through an 'O'-ring seal. The latter construction may be somewhat simpler than that of a 90 t.p.i. screw fitting.

Unfortunately, no reliable figures have been published for the performance of Sutton's still. In view of the fact that the EHP-EHS mixture does not wet the column, the Fenske[75] equation, when applied, showed an apparent separation of only 1.1/4 plates for the whole system. The performance of one column alone was similarly calculated to be 0.5 plates, whereas in practice it would have been near 1.0 when processing a normally-wetting distilland. Hence by inference the complete assembly might be expected to be equivalent to about $2\frac{1}{2}$ plates.

Mair, Pignocco and Rossini. A fifty-stage still was described in 1955 by Mair, Pignocco and Rossini,[80] comprising a pot evaporator, and a sloping column rectifying section basically similar to the Madorsky, Bradt and Strauss apparatus. Mixtures of paraffins in the range C_{18}-C_{22} were separated successfully in this apparatus at a vapour pressure of some 30 micron Hg. with a reflux ratio of 55:1.

The purification of 2.8 l. of oil mixture required however, some 1,900 hours of distillation.

Melpolder, Washall and Alexander. In the same year, Melpolder, Washall and Alexander[81] published notes on a 20-stage countercurrent assembly consisting of one 1,250 ml. pot and 19 smaller pots in series with it, fitted with transfer tubes for distillate and reflux. The pots were of a very simple type, described as early as 1922, in which condensation takes place on the upper portion of the pot walls and distillate is withdrawn through a side tube. Each separate pot is run at a controlled temperature and stands in an asbestos jacket reaching up to the level of the condensing area. As is usual, distillate is led to a higher pot, while residues are displaced downwards towards the large pot at the bottom of the assembly.

Using an EHS-EHP mixture, the still reached equilibrium in about 16 hours and gave about 0.8 theoretical plates per pot.

The still was employed for the separation of Eicosane wax into its main constituents. The charge was 1,500 ml. and distillate was withdrawn at a rate of 28 ml. per 24 hours, with a reflux ratio of 30:1.

Bearing in mind Hickman and Trevoy's work on torpidity, it is curious to find that these unstirred pot

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still stages can give a separation of 0.8 plates. The answer may be that appreciable reflux takes place on the pot walls, and that re-evaporation occurs from the clean moving film of refluxing material. Hence, it may be difficult to estimate the real effective distilling area in order to calculate the separation by means of the Fenske equation.

Robinson. An interesting variation of the multi-effect has been patented by Robinson.[82] The feed flows downwards as a film over a series of heated inclined planes, and distils on to a moving condensing surface parallel to each evaporator. The moving

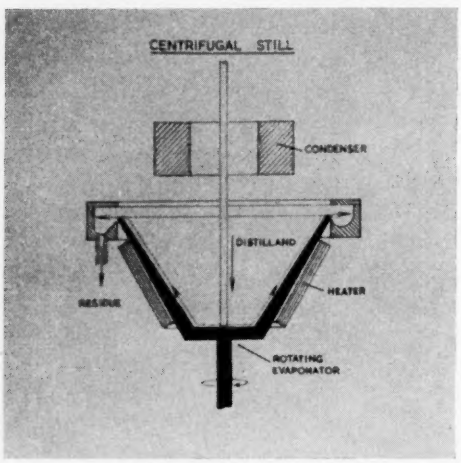

Fig. 15. Showing the principal elements of a centrifugal still.

condenser takes the distillate to a higher stage while the residue passes to a lower stage, and it is claimed that efficient distillation results from the continual renewal of the condensing surface and from the maintenance of a uniform evaporator-condenser gap.

The apparatus has been designed for the separation of isotopes. It could presumably be operated at a lower thermal hazard than the pot cascade fractionators. The author of this paper feels inclined to doubt whether the uniform distilling gap is of real advantage, however, since most commercial apparatus operate satisfactorily with a fairly wide range of molecular paths.

CENTRIFUGAL STILLS

Working Principle and General Characteristics

Interest in molecular distillation as a commercial process, stimulated by the advent of large falling-film stills, led to demands for bigger handling capacity, better fractionation and reduced thermal hazard in the apparatus.

Falling-film units could not be scaled up indefinitely without increasing the distilland contact time and, hence, the thermal hazard. A major design change was therefore necessary. By 1939, a new type of still had been evolved, where the evaporator surface took the form of a rotating disc. The distilland, fed to the centre of the disc, was flung outwards by centrifugal force as a thin fast-moving film, see Fig. 15.

At once, exposure times and film thicknesses could be cut to a fraction of their former values, and the way was open to the development of high-capacity plant.

In practice, the greater complexity of the centrifugal design introduced many new problems which had to be overcome before the stills became a commercial proposition. For instance, the evaporator had to withstand high rotational speeds without distortion, the rotating parts had to be equipped with efficient seal units and a heating system had to be developed which would cope with a moving evaporator. Yet the rate of progress was such that, by 1941, D.P.I. were able to replace all their falling-film stills by centrifugals[85] with 32-inch. evaporators.

The greater part of the work on centrifugal stills was in fact carried out by Hickman and his associates at D.P.I. A number of British Patents has been taken out by Burrows[109,110] but the main stream of ideas seems to have come from the United States.

Design of Major Still Components

The Evaporator Body

Shape, Size and Material. The original flat spinning disc evaporator has a maximum practical diameter of about 1 ft. At greater diameters, the centrifugal force tended to pull the distilland film into a series

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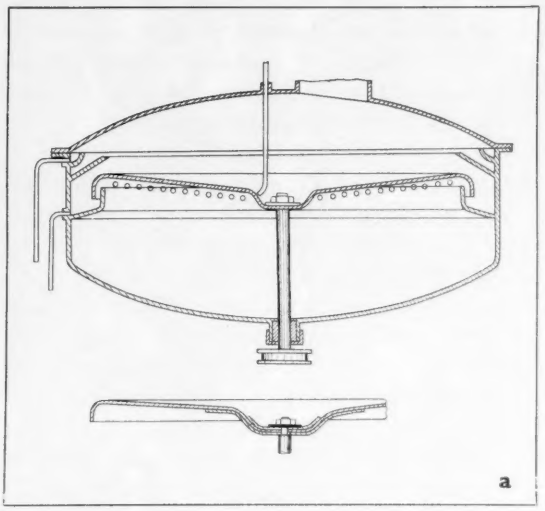


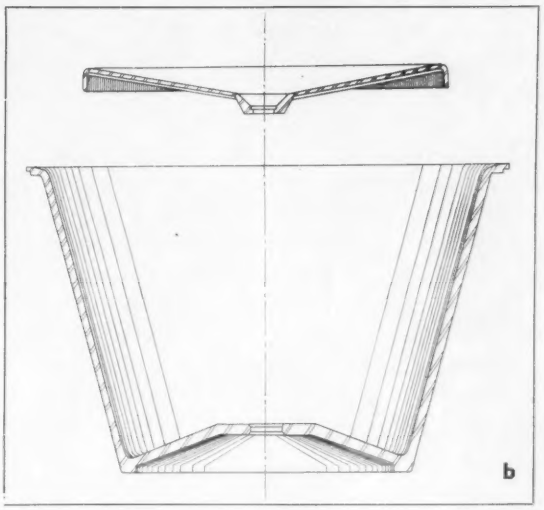
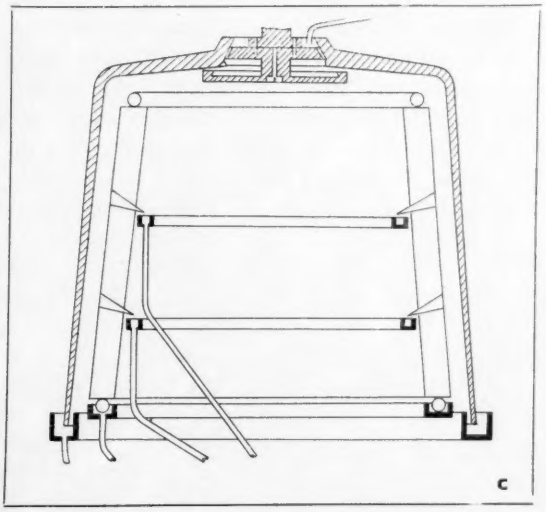
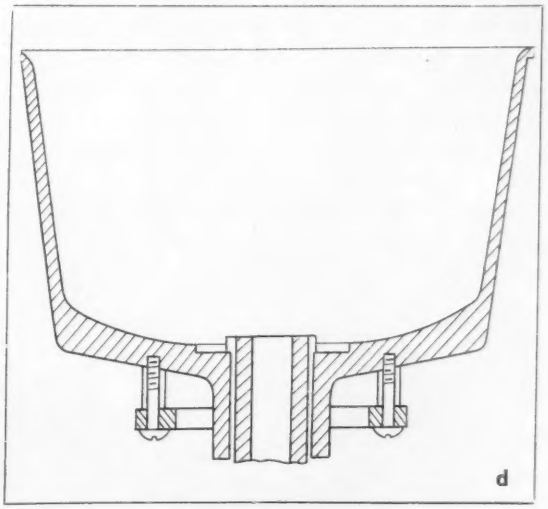


Fig. 16. Various types of centrifugal evaporators: (a) Early spun evaporator; (b) heavy-cast type, of improved heat transfer capacity; (c) inverted 'flowerpot' pattern for easy cleaning; (d) narrow-angle 'flowerpot', giving increased exposure time.





of radial streaks, so that the total area of the evaporator was not utilised efficiently. Reducing the speed of the disc or increasing the flow of distilland to ensure a continuous film at the outer part of the evaporator, gave rise to poor conditions in the central area, where the distilland formed thick layers which failed to reach equilibrium.

The problem was overcome in larger models by providing a cone-shaped evaporator, the area of which increases less rapidly with radius than that of the flat disc. The sides of the cones became progressively steeper with each increase in the diameter. Thus, the small laboratory still[86] fitted with a 5-inch. diameter rotor shows an angle of roughly 150°, the intermediate sizes vary around 130°, and the largest stills have a 'flowerpot'-shaped evaporator with sloping sides subtending only some 10°-20° to the axis, see Fig. 16.

It was essential for success, to construct the rotary evaporators accurately so that the surfaces would rotate smoothly at temperatures up to about 250°C. Distortion at working temperature caused the distilland to channel or char, while splashed oil often landed on the condenser and contaminated the distillate. In the search for a reliable method, rotors were fabricated from steel, spun from aluminium, stamped, or cast and machined. At first, spinning was claimed to give the best results,[87] since it was fairly easy to get good dynamic balance on a small-diameter shallow cone but, with thin metal evaporators, considerable difficulty was experienced from local overheating.

Since the metal provided no adequate thermal sink, surface temperatures were variable and control therefore more difficult. Losses of 33% were reported during routine distillations of Vitamin A. When the poor heat distribution became apparent, heavier evaporators of high-conductivity metals were introduced and as a result thermal losses could be reduced to half their previous values.

A 1950 patent[88], for example, claimed a Vitamin A recovery of 84.3% in a still using a heavy aluminium rotor, and suggested other suitable conductive materials including gold, silver and laminated metals. Most of the massive rotors are cast and machined, as this method gives a true steady surface reasonably free from temperature distortions. The 5-ft. evaporator, probably the most important industrial size in use at present, has an average wall thickness of about $\frac{3}{4}$ inch, tapering slightly towards the rim. The 32-inch. rotor, a standard intermediate size, has a $\frac{1}{4}$-$\frac{1}{2}$ inch wall, and generally, smaller rotors measure around $\frac{1}{4}$ inch.

Surface Conditions and Finish. The surface finish of a centrifugal evaporator is perhaps less critical than that of a falling-film column, since in general the centrifugal force is sufficient to spread evenly all but the most difficult distillands. In the 5-ft. still,[76] for example, the evaporator rotates at about 400 r.p.m., exerting a force of about 130 *g* normal to the rotor surface. Forces of the same order are available in smaller stills, running at appropriately higher speeds, and with all but the shallowest cones, the centrifuging action effectively prevents splash or bubbles from leaving the distilland surface.

Surface finish, however, does affect the rate at

Table II

Apparatus	*Raw Material*	*Tocopherol potency*	*Distillate potency*	*Recovery in Distillate*
Falling film still	Washed cottonseed oil	0.85 mg./g.	30 mg./g.	65%
,,	,,	,,	15 mg./g.	94%
6-inch. Centrifugal — new rotor	,,	,,	30 mg./g.	70%
6-inch Centrifugal — partly carbonised rotor	,,	,,	68 mg./g.	90%

which dirt and carbonised material accumulate on the rotor, and for this reason it is usual to aim at a smoothly machined inside surface.

In practice, a very slightly carbonised rotor often gives better results than a completely new polished surface, as can be seen from the results given in Table II.

This may possibly be due to the formation surface. This may possibly be due to the formation of a chemically inert skin on the metal, to increased film turbulence caused by minute carbon particles on the surface, to a relative increase in the infra-red emission, or to a combination of these factors. On the other hand, heavy carbonisation of the rotor is undesirable, as not only does a large and variable thermal gradient develop across the layer of dirt, but the dirt itself accumulates unevenly, forming irregular ridges which may break up the distilland film into ragged segments.

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Hickman's 5-ft. still incorporates an automatic cleaner, which draws a few short ends of stiff steel wire up and down the evaporator surface on a screw thread and continually removes any lumps or thick surface deposits, while leaving the initial thin layer in position. Naturally, the rate of accumulation of dirt depends very much on the material handled. In the distillation of low-potency fish oils—such as cod liver oil—for Vitamin A production, it is customary to remove the evaporator completely after about a week's continuous use and fit a clean one for the next week's work. For distillation of cleaned or refined oils, or fairly clean plasticisers, on the other hand, it may never be necessary to remove the evaporator, sufficient clearance being effected by the wire brush.

Distilland Layer Thickness and Exposure Times. The distilland layer on a rotary evaporator is much thinner than on a falling-film evaporator. Depending on viscosity and rate of flow the thickness is likely to be in the 0.01-0.1 mm. range for most sizes of centrifugal still. Some workers [127,128] have quoted still lower figures. For the 5-inch. laboratory still,[86] the authors quote 0.01-0.10 mm. at the periphery, while for the 5-ft. still[76] values from 0.04-0.08 mm. are given. As a comparison, the Hickman falling-film cyclic laboratory still[45] gives a film thickness of about 0.25 mm

Exposure time is even further reduced than film thickness. In the 5-ft. still, for instance, Hickman found that a glyceride pumped at 750 kg/hr. took 1.2 seconds to traverse the evaporator. In the 5-inch. still a similar oil took about 0.2 seconds, and in the 14-inch. still rather less than 1 second, as against 20 seconds in the small falling-film still. The total decomposition hazard[79] for a complete distillation of average material is thus about one-tenth to one-twentieth of the value applying in falling-film distillation.

Occasionally, the very rapid passage of distilland across the small stills may give insufficient time for equilibrium to be established. In evaluating a process subsequently involving distillation on 5-ft. stills, it may be more convenient to employ a laboratory still giving the same film thickness and exposure time as the full-scale plant. For this purpose a 6-inch. frusto-conical evaporator the sides of which subtend only about 8° to the axis, running at speeds around 1,400-1,500 r.p.m., provides an appropriately slowed-down film with a delay of several seconds. Such apparatus is not commercially available, however, and usually has to be constructed individually in the laboratory. An aluminium saucepan, with the handle removed, makes a surprisingly good basis for a rough laboratory-model evaporator of this kind.

A coiled-strip evaporator[89] has been suggested, shaped like the mainspring of a clock and rotating about its centre. Distilland fed to the centre spirals outwards to the far end, and is thus exposed for some considerable time as a thin film. Such an evaporator is, however, less manageable than the frusto-conical form, and both heating and condensing are made more complicated if conditions are to be genuinely short-path. Normally, it would appear to be most satisfactory to stick to the flower-pot shape and use an appropriate angle for the sloping side to give the required film speed.

Heating of the Evaporator

One of the major difficulties in constructing a

reliable centrifugal still is to maintain the distilling surface at a suitable temperature and to control the latter accurately. Most of the centrifugals in operation today employ infra-red heating of the rotor, on account of its simplicity and reliability, though many other methods have been suggested in an attempt to improve the overall thermal efficiency of the process.

Resistance Heaters Attached to the Evaporator. Electric resistance heaters have been fitted to the outer surface of the evaporator in a number of designs.[86,90–92,110] This method has the advantage that the surface temperature of the elements is kept down to roughly that of the distilling surface, and hence losses due to radiation from the back of the heaters are quite low. Further, there is little risk of the organic vapours present in the vacuum chamber being decomposed on the surface of the heaters. However, attached heaters have the serious drawback that the power supplies must be fed through slip-ring gear on the rotor shaft. The slip-rings may be placed inside the vacuum chamber, as in the Hickman 5-inch. laboratory centrifugal still,[90] or the leads may be passed through electrode seals to rings outside the vacuum system.[91,92]

The external slip-ring gear is preferable, as under vacuum conditions there may be greatly accelerated wear on the brushes. In any case, it is more convenient to be able to service the brush gear outside the chamber without having to break the vacuum.

The resistance elements may be embedded in a cement mass,[86,90] wound on mica formers and applied to the outside of the evaporator by means of low-expansion metal bands[92] or, formed from a magnesium oxide-filled metal-sheathed cable wound directly on to the rotor. In all cases where any portion of the elements or power leads is exposed within the vacuum chamber, however, it is necessary to use relatively low voltages in order to obviate the risk of flash-over. If operations are likely to be carried out which involve heating at pressures up to 1 mm. Hg—and this may sometimes be the case if degassing is carried out in the still—it is safer not to exceed about 30 V.

The sheathed cable heaters, on the other hand, may be run at full mains voltage if the winding is made in one continuous length with the ends brought out to external brush gear. This is a useful arrangement, as it enables smaller diameter conductors to be used for a given wattage.

Although attached heaters are an attractive proposition for small-scale work, it is not very practical to use them for rotors much over 18 inch. in diameter. Firstly, it becomes difficult to achieve dynamic balance on large rotors. Secondly, it is often desirable to vary the heat input over different zones of the rotor and this involves more complicated windings and multiplication of the brush gear. Finally, it is not easy to make provision for rewinding a large rotor in the event of heater failure. On a small scale, metal-sheathed heater cable may actually be built in the cast alloy walls of the evaporator,[110] and for experimental work the whole assembly may be regarded as expendable. For a 5-ft. production rotor, on the other hand, the cost would be prohibitive.

Heating the Distilland Layer Directly by Radiation. Instead of relying on heat transfer to the distilling film by conduction from a heated evaporator, it has been proposed to subject the film to the radiation from an infra-red source.[93] This involves projecting the infra-red radiation through the back of the condenser, which must itself be transparent to infra-red, on to a film of distilland sufficiently thick to be an effective infra-red absorber.

A rather similar idea, though even more elaborate, is Schlesman's suggestion[94] to use radio-frequency heating of the distilland vapours at specific wavelengths such that energy would be absorbed preferentially by one molecular species, other species being selectively condensed.

Heating the Evaporator by Heat-Exchange Fluids. Perhaps more practical than these ideas are other means for heating the evaporator itself in an otherwise conventional arrangement, One such scheme employs a hollow evaporator[95], through which a heat transfer fluid is circulated. From the temperature control point of view, fluid heating seems a good plan, especially as it can utilise cheap sources of heat in the boiler section. There are difficulties

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with the scheme, however. If the boiler is situated outside the vacuum system and the fluid medium remains at atmospheric pressure, then the double walls of the evaporator must be vacuum-tight and adequately strong to withstand the internal pressure. With relatively thin-walled cast-alloy evaporators, these conditions are not easily obtained. On the other hand, if the heating system is connected to the chamber and reduced to chamber pressure, the transfer liquid is likely to be at least slightly volatile at its working temperature and may contaminate the distillates.

Other Methods of Heating the Evaporator. Radio-frequency heating of the evaporator would require a disproportionately large and costly ancillary plant. Magnetic braking[96] seems to present quite a practicable alternative to the normal heating methods, power from the rotor drive motor being transformed into heat in the rotor itself by its motion in a magnetic field. For a normal range of available power, a magnetically braked 5-ft. rotor would require a drive motor of about 100 h.p. and a correspondingly heavy shaft assembly.

At present it would appear that centrifugal still construction has tailed off with the completion of the existing installations, so that further work on new heating methods may not be considered worthwhile as long as the existing means are known to answer the requirements fairly well and to operate without a great deal of attention.

Heating the Evaporator by Stationary Radiant Heaters. The 5-ft. stills, described in very considerable detail by Hickman in his 1947 paper,[76] simply employ a nest of Calrods arranged round the evaporator, backed by some form of thermal insulation. Calrods are a brand of oxide-filled, Inconel-sheathed, electric resistance heater withstanding thermal and mechanical shocks well. They are similar in principle to the Metrovick 'Redring' elements used in electric cookers in this country.

In one embodiment of the Hickman 5-ft. still, the Calrods are arranged to form three separate zones or banks, so that the distilland temperature rises in three distinct steps from the centre to the rim. Each heating zone has a corresponding condenser zone, and the three condensates pass down into sight-glasses near the operator's panel.

The rates at which the sight-glasses fill up may be checked from time to time by closing valves situated below the glasses and from the readings the operator decides settings for his heater Variac controls in order to maintain the three rates at predetermined levels. For long runs on materials of fixed properties, this simple method works quite well, as there are no changes in the thermal load once equilibrium has been attained. Nevertheless, the thermal efficiency is not very high and it is normally sound practice to install heat exchangers to extract the waste heat from the residue oil and, occasionally, from the condenser assembly.

Thermal Efficiencies of Stills. An early patent[97] of Hickman's asserts that the maximum thermal efficiency of a flat disc evaporator-condenser system is about 10-12%, most of the losses being represented by heat transfer to the condenser cooling water. To reduce these losses, it was proposed to use highly polished evaporating and condensing surfaces which would not absorb infra-red radiation. Further, the condenser was arranged to rotate so that the distillate was kept as a very thin film and was also substantially non-absorbing.[200] Sufficient cooling of the condenser was obtained by continuously recirculating cooled distillate from the external receiver over the rotating condenser. This idea was useful for stills employing plane disc evaporators, but is not really suitable for the frusto-conical or flowerpot evaporators subsequently found necessary.

In fact, with a highly polished static tube nest condenser located inside a flowerpot evaporator, the thermal efficiency probably approaches 30% without the need for additional rotating parts. Further improvements may be made by running the feed and residue oils through a heat exchanger, either a type stationed outside the chamber as is normal in practice, or a type where heat from the outer portion of the distilling surface is transferred to the centre part near the oil feed, by means of an auxiliary liquid.[95]

It is also possible to run the feed oil prior to

treatment through the condenser, *in lieu* of cooling water. However, with all heat-exchange systems the thermal hazard is increased and the thermal efficiency must be weighed against overall recovery.

Finally, yet another arrangement due to Hickman deserves mention, on account of its ingenuity, see Fig. 17. Here the vaporising surface and condensing surface are formed by the two-opposite ends of a single rotating vacuum chamber.[98] Since the outside surface of the ends are exposed to atmosphere any means of heating—such as gas or oil—may be used on the evaporator. Centrifugal p-trap seals allow the

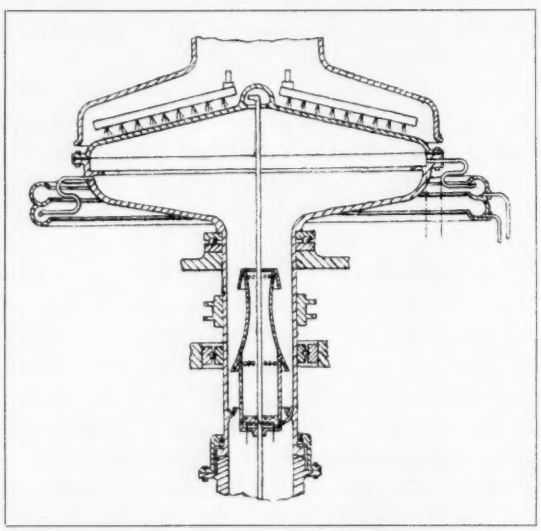

Fig. 17. Still designed by Hickman, in which the evaporator may be heated by stationary external heaters at atmospheric pressure.

residue and the distillate to pass out. The diffusion pump is positioned inside the vacuum manifold which rotates with the chamber.

Power Consumption of Stills. Referring to the conditions in the 5-ft. still which by now is accepted as a standard type of centrifugal still, Hickman states in his 1946 review that the power consumption is less than 0.1 KVA-hour per pound of distilland, or from 0.2-0.5 KVA-hour per pound of distillate, excluding the advantage offered by heat exchange. This represented an overall operating cost of about 1 cent per pound per pass of distilland in 1945. Each 5-ft. rotor is capable of evaporating 30 lb./hr. at a vapour pressure of 1 micron Hg or 300 lb./hr. at 10 micron Hg. Most raw materials will stand 10 micron Hg distillation pressure without serious risk of decomposition.

Calculations by the author and his colleagues on the power consumption of small centrifugals with attached heaters agree substantially with the figures published by Hickman, giving a loading of about 200 watt/kg. distilland/hour.

Actual power ratings range from about 500 watt for a small laboratory still, 7 KVA for a 24-inch. diameter rotor, 60 KVA for a 4-ft. flowerpot, to around 120 KVA for a 5-ft. rotor. In each case, the figures represent maximum available power, not average running power.

The Evaporator Drive

Conventional Arrangements. The evaporator is usually mounted on a shaft provided with a rotor-fixing flange at one end and some form of drive system at the other. Usually, the shaft is carried through the wall of the vacuum chamber and a drive motor is fitted externally. This arrangement requires a vacuum-tight shaft seal.

Since the shaft runs in thermal contact with the hot evaporator, the seal and bearings must be capable of working satisfactorily at temperatures up to 250°C. for long periods unless extra cooling is provided in the region of the seal. Hickman does not describe the seal unit used in his 5-ft. stills, but various commercial seals, using polished hard carbon rings or Teflon inserts, could no doubt be employed. The Angus M.1. seal is very satisfactory and inexpensive, and is now available in silicone rubber to withstand most temperatures likely to be encountered. Wherever possible, an oil pool should be established on the atmospheric side of the seal unit, so that a visual check on seal failure is available and at the same time adequate lubrication of the sealing rim is ensured.

Care must be taken that thermal expansion of the hot shaft does not cause seizure of the shaft bearings. Ball races, for example, conduct heat quite slowly

from shaft to outer race, as the balls only make point contact on each face, and may easily seize during the warming-up period of the still. Rollers are rather more satisfactory, and flexible rollers are better still. Light oil may be used round the bearings to improve heat transfer between inner and outer races, but water cooling of the housing itself merely increases the temperature differential.

Alternative Arrangements. Other driving means are sometimes used: In the 5-inch. laboratory still[86] the hot rotor shaft runs on bearings entirely inside the vacuum chamber and is driven by means of a spring belt from a second shaft at room or chamber temperature passing through a conventional shaft seal and driven by an external motor.

It has also been proposed to drive the evaporator by circulating a low vapour pressure fluid through a turbine or a gear motor inside the chamber[111] so that no shaft seal is required or, in another patent, to fit a vacuum-tight sheath between the rotor and stator of an electric motor so that all the rotating parts are contained within the chamber whilst allowing atmospheric cooling of the stator coils and obviating the risk of flashover.

Motors. A type of motor must be chosen which suits the inertia and final speed of the rotor. A d.c. motor that can be slowly brought to running speed would be very convenient, but is not well adapted to automatic control. A large rotor may take ten minutes to reach maximum speed, unless a rather high-powered motor is used, and this delay would probably result in damage to the starting coils of a normal a.c. motor. However if some form of take-up such as a fluid drive, powder clutch, magnetic coupling, etc., is provided in the transmission to even out the starting load, then a small conventional squirrel-cage motor is adequate.

For laboratory units up to 18 inch. diameter, fitted with light alloy rotors, a capacitor-start a.c. motor of about $\frac{1}{4}$ h.p. is sufficient, using a vee-belt external drive to give a slight measure of flexibility.

The Condenser

Designs for Small Equipment. Condensers for small equipment present no particular problem. The laboratory 5-inch. and 14-inch. stills can both be operated in a glass vacuum chamber, the walls of which act as the condenser, with or without external air-blast cooling. The fact that the evaporator

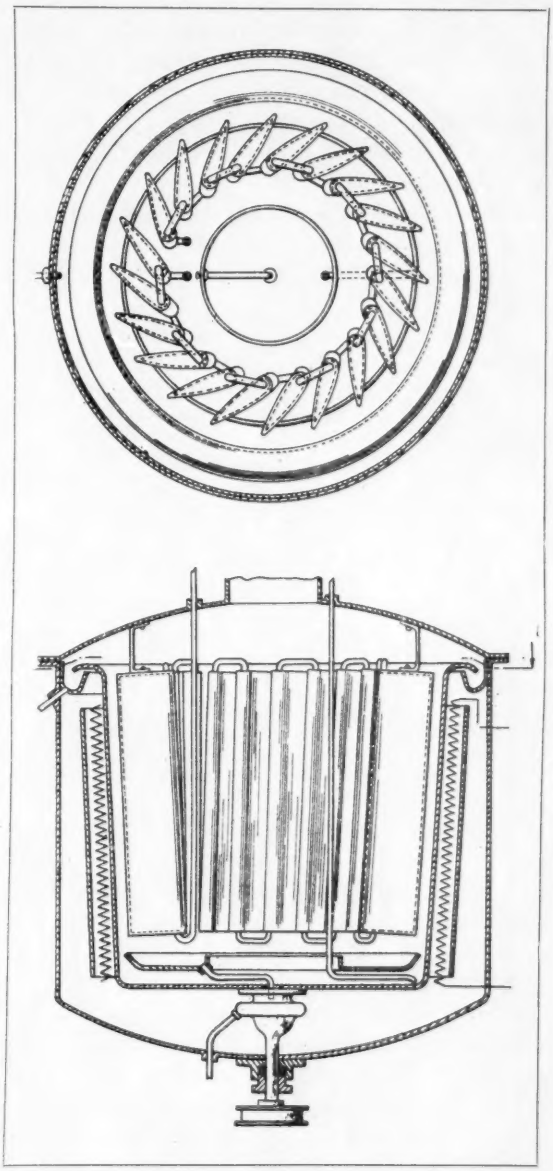

Fig. 18(*a*). Plan and elevation of the Aerofoil condenser. The spaces between the cooling fins form venturi orifices and assist vapour pumping.

condenser gap is thereby fairly long and non-uniform seems to make very little difference to the quality of the distillates, as compared with material condensed over a $\frac{1}{4}$ inch. gap.

During the development period of the centrifugals, direct distillation on to the chamber walls,[87] coils, cooled plates—both static[99] and rotating[97,100]—and various multiple tube assemblies[95] were tried.

Condensing surfaces were arranged in several zones,[101,102] in order to collect fractions of different composition.

Designs for Large Equipment. As the apparatus grew larger, it became increasingly important to ensure that no pockets of gas were trapped in the fairly narrow gap, usually favoured, between evaporator and condenser. Hence the early, solid condensers were discarded and perforated[103] systems, rotating vanes,[104,105] open coils,[93] and nests of tubes,[106] through which permanent gases could pass readily, were employed instead.

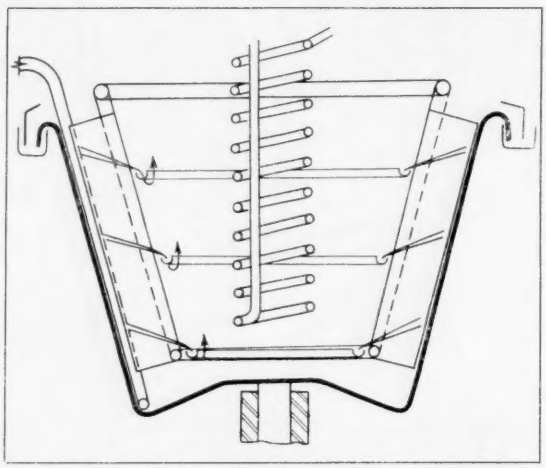

Fig. 18(*b*). Detail of the 5 ft. centrifugal still, showing aerofoil condenser in position. Note the gutters for collecting separate fractions.

The Aerofoil Condenser. Eventually, a design[107] was evolved, see Figs. 18 (a-b), which was not only readily permeable to the gases being evacuated, but was even claimed to exert a pumping effect of its own. It consisted of a number of cooled hollow aerofoil-shaped members, arranged side by side close to the distilling surface, so that the gap between each pair of aerofoils formed a venturi jet. As the mixture of condensable and non-condensable gases passed through each jet, the distillate vapour condensed in a manner similar to that of the vapours of the working fluid in a diffusion pump, while the entrained permanent gases travelled on to the exhaust manifold.

Condensers of this type are used in the 5-ft. stills and facilities are provided for collecting distillate separately from the three heating zones. The condenser is kept fairly hot to minimise heat losses by the evaporator, and a separate water-cooled coil is hung in the centre to remove volatiles that might otherwise raise the pressure in the chamber.

In order to keep fractionation in this system as effective as possible, it is of course necessary to use a short distilling gap so that the two sets of zones correspond. The aerofoil condenser is certainly effective but rather expensive to manufacture. It is doubtful whether its pumping action is of much importance in these days of high speed pumping units. On a laboratory scale, the Vitamins team has attempted to compare the behaviour of a genuine aerofoil condenser with that of a somewhat cheaper substitute fabricated by welding a bent metal strip on to an ordinary round-section pipe, and has not found any practical difference in terms of distillate analysis.

Aluminium and stainless steel are two materials of choice for condensers. After assembly most large tube nests are not very suitable for electroplating, on account of their complex shape and large superficial area. Thus, harmless and non-corroding materials should be used in the first place.

Withdrawal of the Distillate. The distillates, obtained on the three zones of the aerofoil condenser, flow downwards by gravity, and, in the 5-ft. still, pass through the floor of the evaporator *via* a system of pipes and annular gutters.

It has also been proposed to remove distillates from such condensers without running pipes through the evaporator, *i.e.* with the help of pumps [101,103] or by the lifting action of pipes rotating inside the evaporator and inclined outwards at their upper ends.[99] A very simple change in the layout

of the still, on the other hand, makes it very easy to withdraw any number of distillates straight from the condensing zones out through the floor of the still. In the latter arrangement[108] the flowerpot evaporator is inverted with its open end downwards, so that pipes may be run to the condenser directly to the evaporator, and then lift, raising and lowering the hoist several times to remove each component in turn. Dirt, when scraped from the inside of the inverted rotor placed on a suitable support, falls out, rather than in.

The distillates, once drained from the condenser,

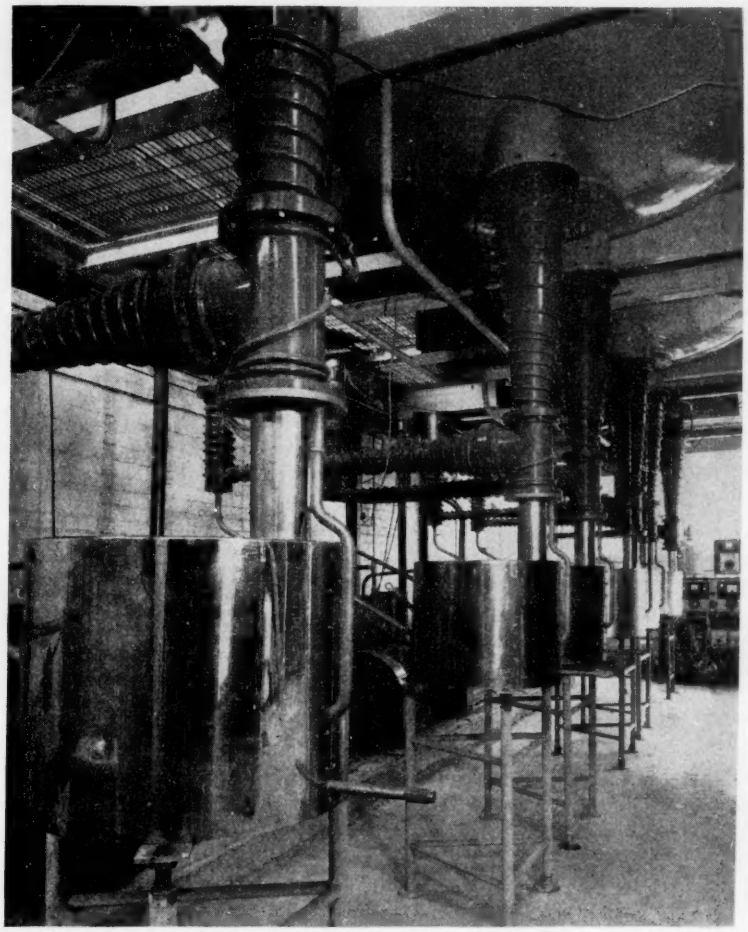

Fig. 19. High Vacuum pumping equipment in a commercial molecular distillation plant. (*Vitamins Ltd.*)

from the baseplate. Using the inverted still layout, it is a simple matter to remove and clean the evaporator, since the chamber lid, drive motor and evaporator lift out as one unit. With the conventional layout, it is necessary to remove the lid, disconnect and lift out the condenser, attach tackle

are conveniently transferred by means of vacuum-sealed gear pumps either to other stills for re-processing or, *via* non-return valves to containers at atmospheric pressure. In early practice, the gear pumps were generally immersed in oil to ensure complete leak-tightness. Oil baths, however, are

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inconvenient, when the pumps are being serviced. In modern practice it is normal to use specially designed pumps which do not require immersion for sealing.

The Vacuum System

Pumps. The growth of centrifugal stills was closely associated with the development of large-capacity pumping units. Many patents dealing with improvements of the vapour pump were granted to Hickman and his co-workers during the 1940's mostly covering fractionating pumps operating on mixed organic fluids and cheap oils.[112–125] The same period saw the introduction of the now familiar 'booster' pump[120] with a vapour jet of comparatively high velocity and an optimum performance in the 10 micron Hg region. This pump was ideal for molecular distillation in the 1-10 micron Hg range as small bursts of vapour released during distillation did not upset the chamber vacuum to the same extent as when a diffusion pump was used. Fig. 19 gives a view of pumping aggregates, forming part of a molecular distillation production unit operated by Vitamins Ltd.

Until fairly recently, the need to cope with large amounts of volatiles has, generally speaking, prevented the use of mechanical pumps where commercial plant was concerned. Two alternative systems are described by Hickman. In the first, a diffusion pump and two boosters are backed by three steam ejectors in series. In the second, one large diffusion pump is backed by a five-stage steam ejector. The diffusion pumps are run on petroleum fractions (DPI 'Myvane' fluids) which are cheaply replaced when contaminated with volatiles. In a typical installation such an exchange may be required once a month.

A paper published by Morse[127] in 1947 gives characteristics for pumps available at the time, quoting work on 32-inch. diffusion pumps with a speed of 30,000 cu.ft./min. at 10^{-5} mm. Hg, then being produced in quantity. He also refers in this paper to the introduction of silicone fluids for diffusion pumps. Although these fluids are of very high stability, they are still liable to contamination by condensed volatiles and require regular replacement. As their cost is high, there is much to be said for continuing with a cheap expendable oil.

As to the sizes of the vapour pumps employed, it is tempting to suggest, as a rough rule, that one diffusion pump of rather less than half the evaporator diameter provides adequate pumping capacity in the 0.1-1.0 micron Hg pressure range. Somewhat smaller sizes can be used if it is permissible to operate in the range from 1.0 to 10 micron Hg and, if the evaporator is a shallow cone rather than a flowerpot.

The recent development of gas-ballast rotary pumps makes it possible to reconsider the use of mechanical backing pumps, since vapour contamination can be dealt with very effectively in a gas-ballast pump. Steam ejectors are often more expensive to install and run than a corresponding ballasted pump, and for medium-sized installations, in particular, the gas-ballast pump is well worth considering.

Chambers. The design of chambers for molecular stills is a fairly straightforward vacuum engineering task, chambers generally being welded from sheet steel, with large flange connections and 'O'-ring seals. In very small units for laboratory research work, it may be more convenient to use a glass chamber in order to watch the progress of distillation and the behaviour of components. The latter principle is used in the Hickman 5-inch. still and in various experimental models made in the laboratories of the author.

Where a glass chamber is employed it is desirable to attach the vacuum manifold, pipe, fittings and evaporator drive to a metal plate and to arrange for the chamber to seal on to an elastomer seating on the plate so that the chamber can be easily removed without any disconnection of other components.

Trapping of Vapour. Generally, some elementary form of vapour condenser is inserted between the chamber and the diffusion pump. In the 5-ft. stills a grid of small-bore copper tubing, water-cooled, is sufficient to remove semi-condensables not caught in the centre coil of the condenser. In small laboratory installations fitted with conventional diffusion pump/rotary pump trains, it may be worth

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while introducing a carbon dioxide trap in order to reduce the frequency of pump oil changes.

Pressure Measurement. For measuring the vacuum obtained, the Pirani gauge is almost universally used, since it gives a continuous indication of total vapour pressure. Alternatively, a thermo-couple gauge may be employed.

Design and Performance of Complete Stills

The preceding notes contain many references to the 5-inch. and 5-ft. stills of Hickman. Not only are these stills good examples of a laboratory and production model respectively, but the articles describing them are two of the few publications reporting in detail on centrifugal apparatus. Far less construction work appears to have been published by individual laboratories than is the case with falling-film or pot stills for example, and this is very probably due to the greater complexity of the apparatus.

The interested reader is referred to the original articles, since they contain a great deal of information too voluminous to be included here, but a few brief notes will be added in order to give a proper idea of the layout and operation of each.

The Individual 5-Inch. Laboratory Still (see Figs. 20-22). The evaporator, oil feed pump and reservoirs are disposed inside an inverted glass bell-jar hanging from an upper metal plate. The plate is supported from a metal cabinet containing the controls, and meters and it also carries the motor.

The evaporator is rotated on a horizontal shaft by a spring-belt drive, and oil contained in the bottom region of the bell-jar is pumped to the centre through a small gear-pump. The oil spins over the rotor surface and is caught in a stationary annular gutter surrounding the outer edge of the former, from which it runs down over a small cooler into a reservoir half-way up the bell-jar. During its passage over the evaporator at fore vacuum the charge is partly degassed, and frothing is suppressed by the shear forces on the rotor. Several cycles may be necessary at progressively higher rotor temperatures, the charge being allowed to pass from the reservoir into the bottom of the bell-jar after each complete cycle. The temperature of the oil film is measured with a small thermocouple element riding in a slight lip at the rotor rim, and heat input to the cast-in heaters is regulated with a Variac. When degassing is complete, the chamber pressure is further reduced with a booster-type oil vapour

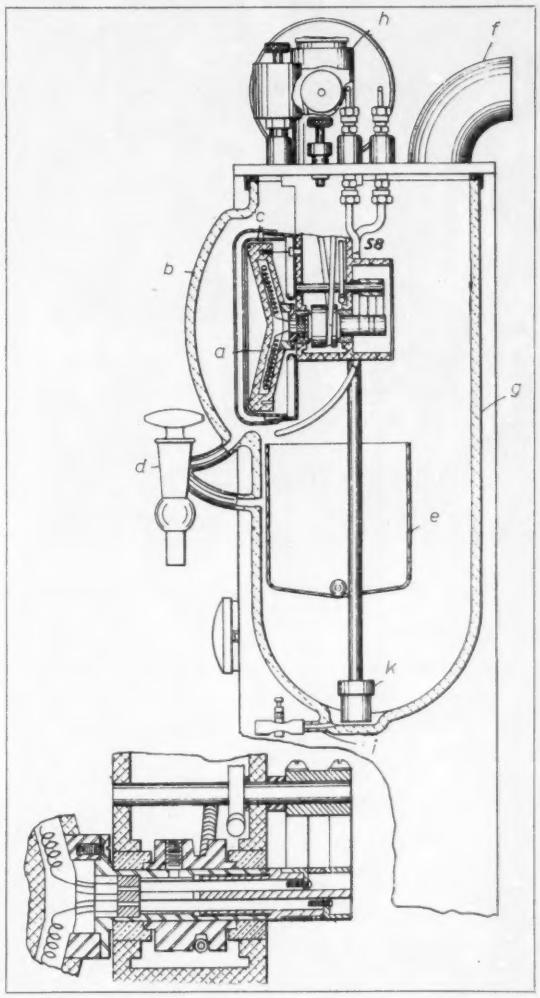


Fig. 20. Hickman's 5-inch. laboratory still. *Legend:* (a) Evaporator, with cast-in resistance heaters; (b) condensing surface; (c) residue gutter; (d) distillate withdrawal cock; (e) residue container; (f) vacuum manifold; (g) glass vacuum chamber; (h) shaft seal unit with belt drive to rotor; (i) residue drain and feed inlet; (k) feed pump.

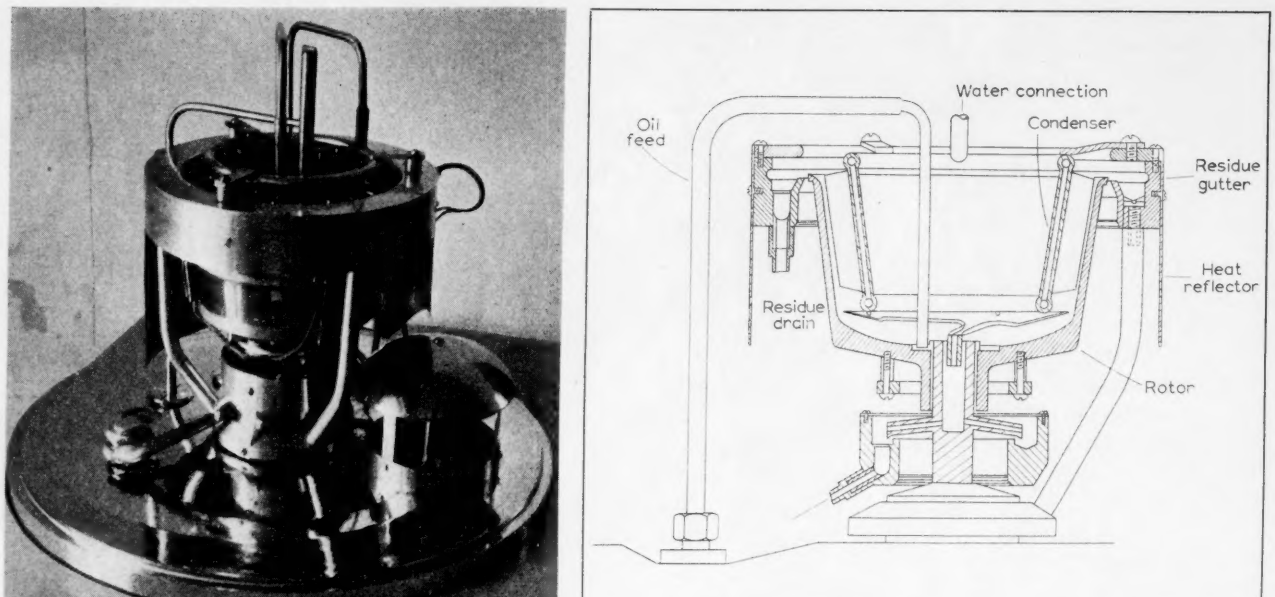
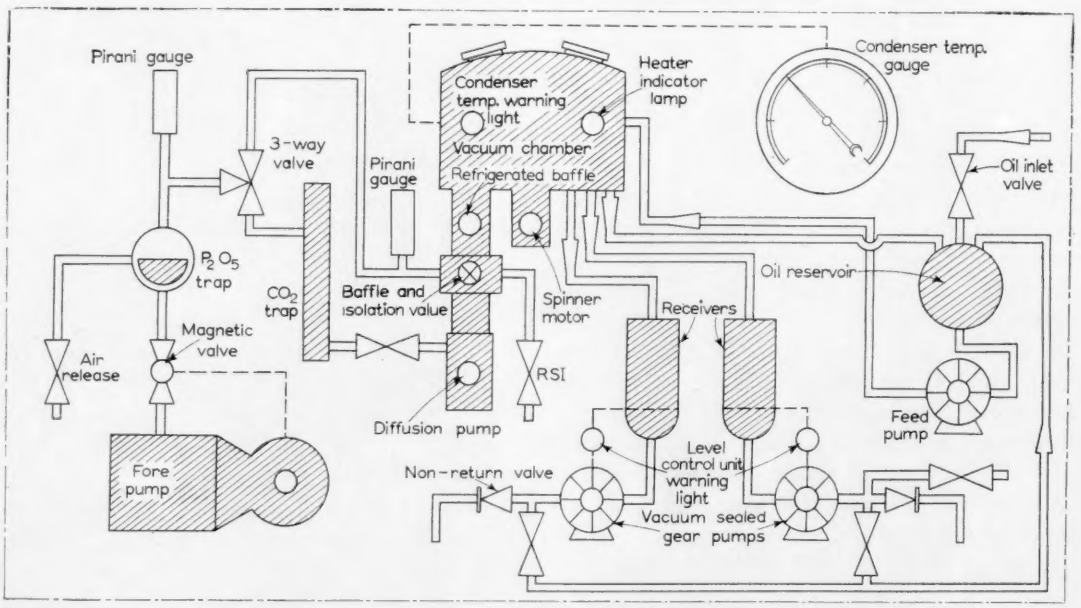


Fig. 21. Photograph and line drawing of 6-inch. still developed by Vitamins Ltd. for batch or continuous operation. The long exposure time available makes the still suitable for the study of processes to be developed on a commercial scale using large stills.

Fig. 22. (Below). Layout of graphic control panel for the same still designed to assist rapid fault finding.



pump and distillation takes place from the distilland to an area of the bell-jar wall, immediately facing the evaporator, from whence it runs down to a glass cock arranged at the front of the still. Distillate may then either be withdrawn, or allowed to reflux into the bottom reservoir.

Some operating data are given, for example: The elimination curves of celanthrene red and dimethyl-

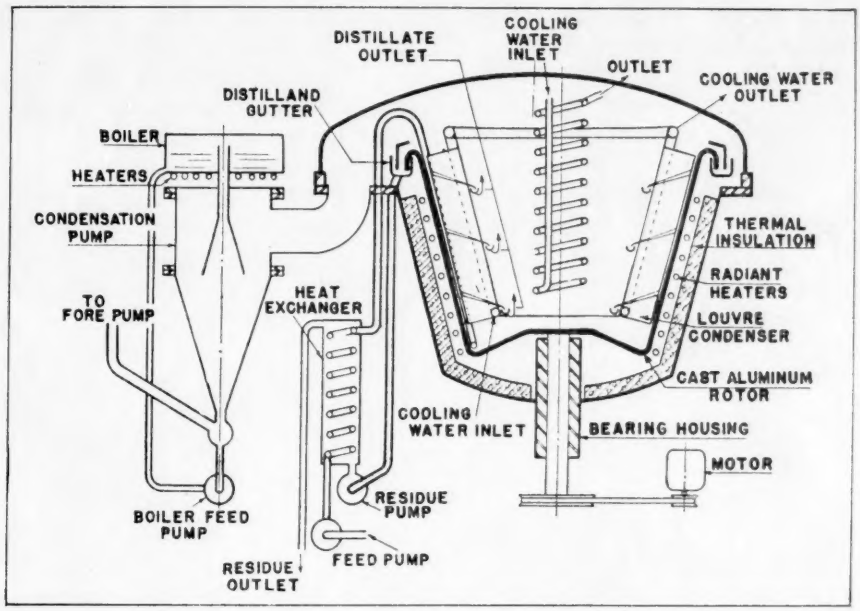


Fig. 23. Diagrammatic elevation of a 5 ft. molecular still.

anthraquinone are shown to compare favourably with those from a falling-film still at throughputs in the range of 35-100 g./min. The separatory power is quoted as roughly 1 theoretical plate, at distillation rates up to about 180 ml./hr. Soyabean oil has been distilled up to 400°C without decomposition.

The 5-*Ft. Still Production Installation* (see Fig. 23). A typical production installation contains stills of various sizes: 5-ft. stills, for processing the raw material, and 32-inch. and 14-inch. stills for subsequent treatment of the primary distillates. The ancillary equipment will include heat exchangers, continuous flow degassers, material storage, and a large vacuum pumping installation.

Feed material from the store tank passes through a heat exchanger, picking up heat from undistilled residue oils and thence the hot feed is sprayed into a tower maintained at about 2 mm. Hg pressure from the main steam ejector manifold.

Primary degassing takes place in this tower and the feed oil is then pumped into a second tower maintained at about 0.01-0.10 mm. Hg pressure, for further degassing. Flow rates of the oil are controlled by vacuum-sealed gear pumps and observed with Rotameters, and will be in the range of 300-1,000 kg. per hour per 5-ft. still. Often a third stage of degassing is employed. This stage is maintained at 0.01-0.001 mm. Hg by means of booster pumps, and a condenser in the vapour manifold continuously removes a low-boiling fraction from the feed oil. Thorough degassing is of critical importance.

The degassed oil is pumped into the rotating evaporator and, as in the smaller stills, flashes over the surface, being caught in an annular static gutter provided with a temperature-sensing element. Distillates collect on each of the three zones of the multi-leaf condenser and are removed separately.

They may then be combined or recirculated according to various possible schemes, *e.g.* those of Fawcett[77] or Frazer.[78] Various other linkages are quoted in Hickman's paper, whereby distillates are re-processed in the smaller stills to give maximum fractionation with minimum thermal hazard.

As with the small still, the fractionating power does not normally exceed 1 molecular plate per pass. It is possible to improve the performance slightly by interposing open-mesh wire barriers,[129–131] between rotor and condenser. Such a barrier provides a continuous partial reflux, as the condensate collecting on it drops back on to the floor of the rotor and thus it helps to reduce the risk of splash entrainment. Alternatively, the condenser zones may be internally arranged to feed distillates back to points on the rotor surface[132] such that counter-current redistillation takes place and fractionation is improved.

Some performance figures are quoted for a number of materials: Vitamin A esters, for example, in a single-pass distillation of fish-liver fat, are concentrated about five-fold at 70% yield, while 25% remains in the residue and is presumably further distilled. Sitosterols from vegetable oils are concentrated about eighty-fold in one pass, at 90% yield.

Alpha-tocopherol with a molecular weight around 430, is separated almost completely from gamma- and delta- tocopherol (respective molecular weights, 416 and 402) in seventeen distillations.

Again, the performance figures obtained by the Vitamins team and shown in Table II, seem to accord with those of Hickman and demonstrate clearly the improved performance of the centrifugal over the falling-film unit, under good conditions.

Performance figures are still rather hard to find in the literature, but in the experience of the author of this paper these seems to be little doubt that the centrifugal still is a very powerful and effective tool in applications where its complexity and cost are justified. Most of the centrifugals in existence were of DPI origin, but independent installations have been made in the United Kingdom and in Spain.

ROTARY STILLS

General Characteristics. A few stills have been constructed, in which the distilland film is produced on a slowly moving surface, so that centrifugal force plays only a small part in the action. Stills of this kind do not require as careful a construction as do centrifugals, and their components are subject to very little stress during operation. On the other hand, the distilland films obtained are of fair thickness, and the total exposure times may be quite long; thus, rotary stills are mainly suitable either for batch laboratory operation or for the processing of thermostable materials.

Givaudan Still. A typical example of a large-scale rotary still is the Givaudan apparatus,[134] used for the distillation of essential oils.

The main chamber of this still has the form of a closed horizontal cylinder, along the axis of which runs a rotatable shaft carrying a number of metal discs. In between the discs, in the upper half of the chamber, flat water-cooled condensers are arranged. The oil to be distilled is held in the lower portion of the vacuum chamber in a relatively deep layer, the discs being partly immersed in it. When the shaft is slowly rotated, a film of oil is continuously formed on each side of each disc and carried past the condenser plates. Means are provided to heat the discs by an internally circulated heat transfer fluid raised to the desired temperature in an external boiler, or, alternatively the whole charge of oil in the chamber may be heated. In operation oil is admitted slowly to one end of the chamber *via* a continuous degasser and spent residues overflow from a drain at the far end. Under these conditions fractions of differing composition collect on the separate condensers and are passed into receivers for further treatment as required.

Hickman's Design. Other rotary still designs provide for a cylindrical evaporator which is rotated slowly about its horizontal axis. The bulk of the oil is contained in the lower portion of the cylinder and a thin film of the oil is carried around on the inside of the cylinder walls. Hickman claims that high thermal efficiencies are possible with such a cylin-

drical evaporator, if positioned and operated within a jacket fitted with infra-red heaters,[137] because the heat radiated from any part of the inner cylinder surface is largely re-absorbed on the opposite part of the same surface.

Condensers are arranged just outside the open ends of the cylinder, and do not impose any thermal load on the radiant heaters. Distilling molecules have a rather long path to the condensers, but in many cases this may not be important.

Zaugg and Shavel's Still. A batch laboratory still designed on similar lines but with an internal condenser for short-path operation was described by Zaugg and Shavel[135, 136] in 1954, see Fig. 24. It is suitable for 5-50 g. quantities, and the evaporating cylinder is made from glass so that the distilling film can be heated by an external infra-red lamp of the normal commercial pattern. A novel feature is that the condenser can be inserted through a spherical ground joint into the vacuum chamber.

During the degassing period, the condenser may be tilted so that splash or distillates run off its lower end into the evaporator cylinder. When degassing is complete, the condenser is tilted in the opposite direction so that condensed material runs outwards and may be collected as in the sloping condenser pot stills.[22–25]

The evaporator is driven by a magnetic coupling, which runs very easily by comparison with most shaft seal units. Since the distilling layer is relatively deep in stills of this pattern, temperatures are measured with a fixed thermometer or thermocouple arranged to pass through the open end of the evaporator and to be immersed in the main bulk of distilland.

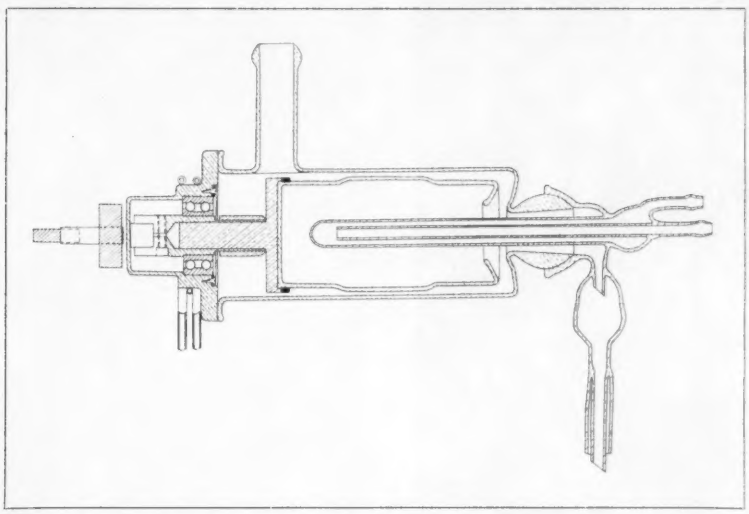


Fig. 24. Rotating barrel still proposed by Zaugg and Shavel. For details see text.

THE WIPED-FILM STILL

General Characteristics. During the last few years a type of still has become commercially available,[138] where the evaporator is a static vertical cylinder, a thin film of distilland being maintained on its inner surface by means of a moving wiper-blade. A condenser is disposed axially down the centre of the apparatus, and take-off pipes run out through the lower end of the chamber.

Apparatus constructed substantially on these lines was described by Hickman and Perry[138] in 1944 and patented in 1948, but the design does not appear to

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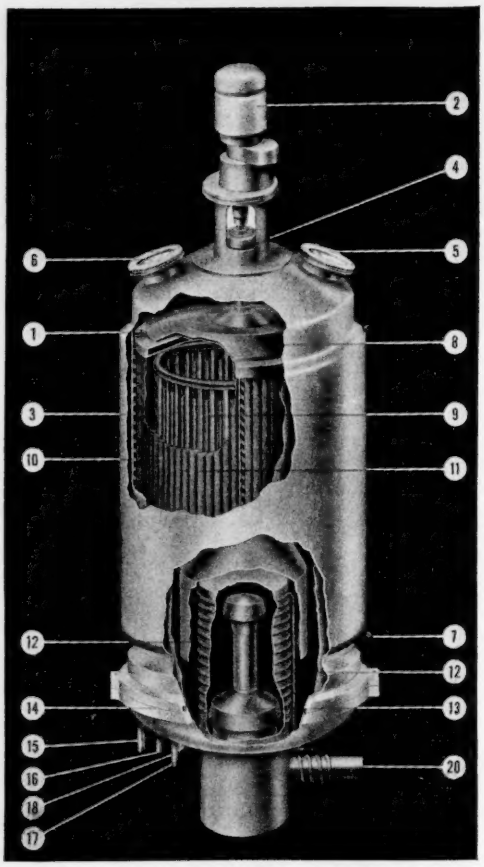

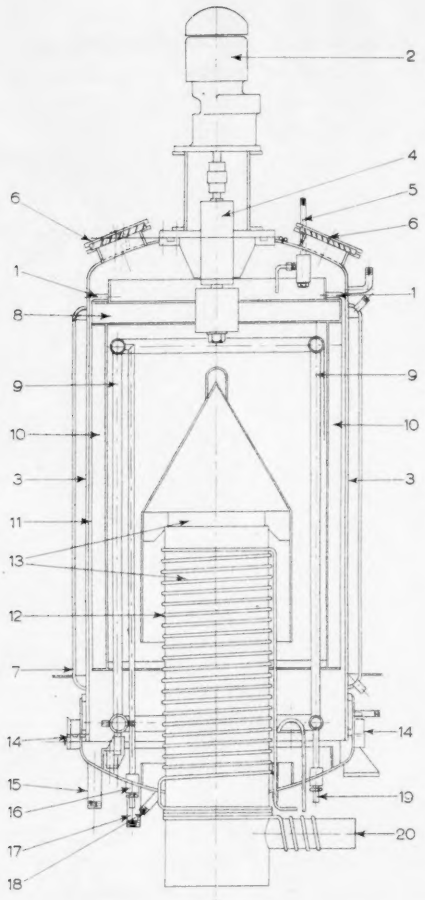

Fig. 25. Wiped film still. *Legend:* (1) Feed nozzle to evaporator, (2) gear head motor (reduced speed); (3) evaporator wall (4) oil (vacuum) sealed stuffing box; (5) distilland feed; (6) slight glass; (7) jacket drain; (8) rotor; (9) vertical tube condenser; (10) carbon wipers for distilland film distribution; (11) entrainment separator; (12) diffusion pump condensing coils; (13) diffusion pump built in; (14) still comes apart for service and cleaning; (15) residue outlet; (16) condenser inlet; (17) distillate drain; (18) condensate drain; (19) condenser drain; (20) to forepump.

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have been used in practice or made available commercially.

The development of a practical still using the wiped-film principle seems to be one of the major advances in molecular distillation since the advent of the 5 ft. centrifugal, for it represents a comparatively cheap still of potentially large throughput, capable of handling all but the most thermolabile materials. Hitherto, there has been little choice in high capacity plant, since DPI, the leading still designers, persevered with the effective but expensive centrifugal type.

Where particularly thermolabile and highly-priced materials such as Vitamin A are to be processed, the use of the centrifugal still is almost certainly justified, but the feeling among chemical engineers—at least in Great Britain—seems to be that molecular stills intended for more general applications would not be widely adopted unless they became cheaper, simpler and more foolproof.

The Arthur F. Smith Still. The Arthur F. Smith[149] still, see Figs. 25 and 26, goes at least part of the way in this direction, although performance figures do not yet appear to be widely published. On account of its comparative importance some details of the still are given below.

The Chamber

The vacuum chamber is a vertical cylinder closed at the ends, the inner walls of which are machined to reasonably true cylindrical form and constitute the evaporator surface. The evaporating area, being part of the chamber walls, is very conveniently heated by means of a jacket surrounding the chamber and carrying a hot fluid medium at controlled temperature. This simple means of heating is a good point, as no parts are at a higher temperature than the distilling surface, and cheap fuels can be utilised at reasonably high efficiency. The chamber is made from stainless steel, and is easily demountable for cleaning, being provided with a flanged joint at the bottom. As in the example of the inverted centrifugal still constructed by the author, the chamber and drive mechanism lift clear off the baseplate and condenser section in one single handling operation. The flange joint employs a seal ring in PTFE or some similar high temperature-resistant plastic.

The top of the chamber is fitted with inspection windows and carries a geared-drive motor which operates the wipers and the entrainment separator.

The Oil Distribution Mechanism

The motor rotates, *via* a shaft seal unit, a flat disc-shaped rotor, within and near the top of, the vacuum chamber. Nozzles are fitted round the edge of the rotor, facing radially outwards and nearly touching the inside surface of the evaporator section. In addition to the nozzles, the rotor carries a number of vertical, spring-loaded wiper blades which make contact with the evaporator wall. The blades consist of a large number of small elements, made of hard carbon or PTFE, and may be grooved at an angle in order to increase or decrease the downward travel of the distilland film, as required. Finally, the rotor carries an entrainment separator. The latter consists of a large number of vertical metal strips, overlapping after the fashion of a venetian blind

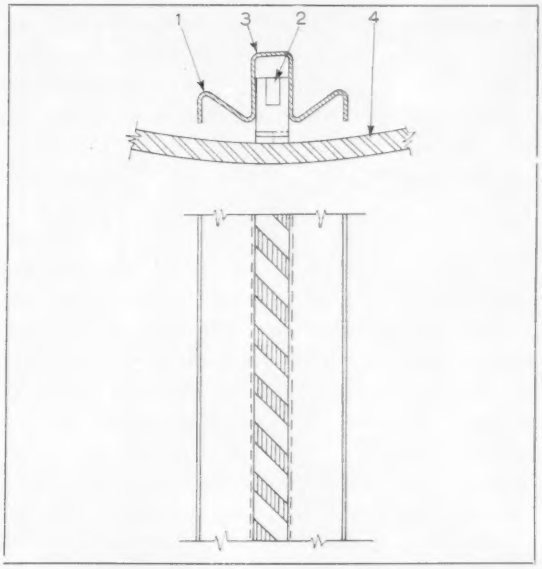

Fig. 26. Wiped film still: Detail of wiper blade. *Legend:* (1) Spatter collection guard; (2) wiper; (3) wiper guide trough; (4) evaporator surface.

on end and rotating close to the evaporator surface in the space between the latter and the central condenser. Should distilland splash from the evaporator towards the condenser, it is intercepted by the rotating entrainment separator and centrifugal force flings it back to the evaporator.

The Condenser

A vertical, cylindrical tube nest condenser is used, with large numbers of vertical pipes all joined to two end-rings. The pipes may, or may not, have additional vertical fins to increase the baffle effect. Occasionally, two condensers are fitted. In these models, the evaporator surface only extends half-way down the sides of the vacuum chamber. One condenser is fitted immediately opposite the evaporator for short-path distillation, and the second condenser is located underneath, running at a lower temperature and collecting a lighter fraction.

The Pumps

The high-vacuum diffusion pump projects almost full-length into the vacuum chamber, so that there are no pumping losses due to manifold friction. An inverted metal cone is fitted over the top of the pump, presumably to prevent spray droplets from falling in.

As with the frusto-conical centrifugals, the pump diameter is usually a little less than half the evaporator diameter. Thus, the smallest model, with a 12-inch. diameter evaporator, employs a 6-inch. diffusion pump. Backing can be arranged to suit conditions. It can be provided either by a steam ejector or a mechanical pump. Also booster pumps may be incorporated. The maker's illustration of the 36-inch. diameter still, for instance, shows a three-stage 9-inch. booster in the backing line.

The Still Assembly

The ancillary equipment is much the same as that of other molecular distillation plant. There are several spray-tower degassers in series, a heat-exchanger to extract waste heat from the residue oil, and Rotameters in the lagged oil-feed lines. Gear pumps are employed throughout to move the distilland, distillates and residue. These useful positive displacement pumps act at the same time as vacuum seals for liquids moving in and out of the chamber.

Stills are claimed to be available as packaged units with evaporator diameters of 12, 36, 48, 60 and 96 inch.* Exposure times as low as a fraction of a second are claimed for the commercial wiper-film stills, so that scaling-up a process designed on a laboratory still would not greatly increase the thermal hazard.

The availability of these relatively cheap laboratory units may well stimulate interest in the incorporation of a molecular distillation step where suitable conditions obtain during the early stages of process development work.

MOLECULAR FRACTIONATORS

General Characteristics. We have noted in previous sections that molecular stills never give separations exceeding 1 theoretical plate per pass. Any attempt to interpose baffles between evaporator and condenser, corresponding to the arrangements in the conventional fractionating column, increases the hazard to the distilling molecules and ceases to make the operation 'molecular'. It was, of course, accepted in the early days[137] that distilling gaps of, say, twenty times the mean free path of the vapour molecules could be used without significant change in the distillates, provided collisions with residual gas were kept at a minimum.

Most fractionator packings, however, cause such large pressure gradients that conditions in the portion of the column remote from the vacuum pump would hardly merit the description of high vacuum.

Nevertheless, the column designers have constructed fractionators of progressively more open layout, and today, there are several patterns avail-

* In addition to the wiped-film stills Smith markets a range of laboratory apparatus including a small stirred pot-still and a type of falling-film still working at feed rates up to 1 l./hr. The falling-film still has a grooved plate evaporator with a 20 ml. hold-up and a long exposure time, *i.e.* six minutes, but since the purpose of this equipment presumably is to explore the distillation of fairly stable materials, this may not prove a serious cause of trouble.

able, intended to cover the no-man's land between high saturation-pressure stills and low-pressure columns. In essence, most of these consist of a vertical column with heated walls surrounding a rotating vertical condenser. Vapours from an evaporator unit at the bottom of the column condense on the central cold core and are flung off on to the heated column walls. Partial re-evaporation takes place, the less volatile fractions returning by gravity to the boiler while the light cuts gradually escape upwards to an external condenser.

Original models including the spinning band column[139] and other rotary condenser arrangements[140, 141, 145] proved to lose separatory power under high vacuum.

Perry and Cox's Brush Still. At the moment, the most promising arrangement seems to be the brush still developed by Perry and Cox[142] from ideas by Hickman[143] and, Perry and Mansing, see Fig. 27.[144]

In this, a rotating vertical condenser is equipped with wire bristles arranged in spiral formation resembling a bottle brush. The stainless wire bristles just touch and sweep the inner surface of a heated vertical column, and the whole condenser assembly is rotated at about 450 r.p.m. A cone stirrer on the lower extension of the condenser shaft dips into the pot boiler at the bottom of the still and keeps the distilland agitated continuously. Operating conditions are fairly critical for a still of this type: Boil-up rate, degree of condenser cooling, heat input and distribution to column walls must all be held within certain limits, but it is possible to operate at comparatively low pressures and still achieve good separations.

The pressure drop down the column is of the order of 100 micron Hg using the spiral brush, and separations corresponding to 7-8 theoretical plates have been reported.

However, at present it seems that for fractionating in the sub-micron range there is as yet no substitute for repeated molecular distillation employing either several individual stills, or compound apparatus where the distillations take place sequentially in one chamber.[146, 147]

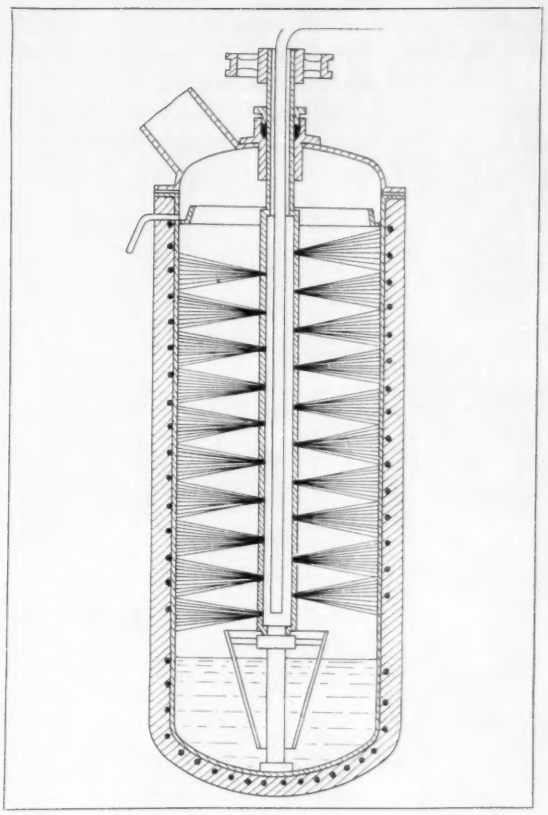

Fig. 27. An early version of the Brush still. Up to date modifications give extremely high fractionating power although the pressure drop along the brush column is usually at least 100 μ Hg.

CONCLUSIONS

Molecular distillation grew during a few years from a laboratory art to a great industry. For the last ten years, however, construction work seems to have been more or less static: The immediate scope of the process, *i.e.* its application to the treatment of vitamins, sterols, monoglycerides, etc., has been fulfilled, but the cost and complexity of the plant have retarded further increases in the existing distillation capacity for relatively cheap materials. In the meantime, studies on materials produced by distillation have led to the development of new and cheaper syntheses, so that it may soon become more economical to synthesise some fine

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chemicals—such as Vitamin A—than to distil them from natural products. The availability of the wiped-film still might tempt manufacturers to use the technique on medium-cost raw materials, but the introduction of a still with improved fractionating power in the 1-10 micron Hg range would be even more important. The wider use, particularly in this country, of molecular distillation as a standard organic laboratory technique would almost certainly stimulate new ideas for the commercial use of the process, as well as giving the laboratory chemist another powerful aid.

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SPOTLIGHT ON VAPOUR SOURCES

THE CONTINUOUS EVAPORATION OF ALUMINIUM IN VACUUM

Summary

LIQUID ALUMINIUM reacts or alloys with the commonly known refractories. Refractory metal carbides have been found to have sufficient resistance to attack by molten aluminium to permit the construction of dependable vapour sources. Sintered carbides of Si, W, Zr, Ti, Nb and Ta were tested and the most rapid disintegration occurred with SiC which reacted to form volatile silicon. Evaporation of silicon could be suppressed by the addition of boron carbide to the SiC. Maximum source life was obtained with TaC. Molten aluminium freely flows over refractories and must be prevented from reaching the surface of the heating element if this is reactive. A carbide coating on a resistance heater rarely protects the heater. A vapour source is described consisting of a carbide plug resting in a cavity of a carbon bar heating element. Aluminium wire is fed on to the carbide plug and evaporation occurs from the upper and vertical surfaces of the plug. The feed rate and evaporation temperature are adjusted to prevent liquid aluminium flowing on the carbon at the base of the plug. Aluminium atoms evaporated in the cavity collide with the heating element and are re-evaporated upwards. Using a 14 mm. cube of TaC and a power input of 10 kW an evaporation rate of 2 g./min. is achieved. The carbon bar can be replaced by a carbon susceptor containing the refractory plug which is heated by a h.f. coil and acts as a vapour reflector. Curves of the vapour intensity distribution show a departure from that of a surface emitter, due to the beaming of vapour atoms from the heater cavity.

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Sommaire

DESCRIPTION D'UNE source d'évaporation consistant en une pièce de carbure, posée dans une partie creuse d'une barre de carbone employée comme élément de chauffage. Le fil d'aluminium est déroulé sur le carbure et l'évaporation prend place sur le dessus et les côtés de la pièce de carbure. Le band d'alimentation en fil et la température d'évaporation sont ajustés afin d'éviter que de l'aluminium liquide s'écoule sur le carbone, à la base du carbure. Les atomes d'aluminium évaporés dans la cavité entrent en collision avec l'élèment de chauffage et sont ré-évaporés vers le haut. Avec 14 mm.^{3} de TaC et une puissance de 10 kW, on obtient une évaporation de 2 gr./min. d'un support de carbone contenant une pièce réfractaire chauffée par HF et agissant comme réflecteur de vapeur. Les courbes de distribution de l'intensité de la vapeur montrent une tendance à s'éloigner des caractéristiques de l'émission de surface, ceci dû à la forme du faisceau de vapeur s'échappant de la cavité de l'élément de chauffage.

Introduction

Vapour sources capable of evaporating large quantities of aluminium are required in high vacuum plant used for depositing thick metal coatings or metallising strip materials in roll form, *e.g.* plastic foils. It is economically desirable to metallise strip materials with a width of three feet or more at speeds in excess of 100 ft./min., and to achieve this it is necessary to have vapour sources that are capable of evaporating several grammes of aluminium per minute, and which can operate for long periods without renewal of the refractory components. This is not possible with the tungsten filament sources which are currently used for evaporating aluminium on front surface mirrors. Attempts have been made to lengthen the life of tungsten heaters by novel source design and the techniques used have already been reviewed by the writer.[1] However, none of the vapour sources described can be used for evaporating more than a few grammes of aluminium before they disintegrate. Two major problems must be solved before a satisfactory source for the evaporation of large quantities of aluminium can be produced:

(1) A refractory material must be found which is capable of withstanding the chemical or alloy attack of molten aluminium.

(2) The vapour source must be designed so that the source of heat energy is protected against attack by liquid aluminium, which freely flows over the surfaces of refractories.

A vapour source is described below in which these problems have been overcome. The development of both the refractory materials and the source construction and experience in their uses has covered some eight years. Needless to say, the final source design owes much to the efforts of many of the author's colleagues.

Reactions Between Aluminium and Refractories

Aluminium evaporates sufficiently fast for most deposition purposes at a temperature of about 1,500°C. At this temperature the metal is a highly mobile liquid which readily wets and reacts with the commonly known refractories. Thus the refractory metals, tungsten, tantalum, molybdenum are dissolved by liquid aluminium. Carbon reacts with aluminium to form yellow carbide crystals. The carbide surface layer which initially forms is not a barrier to further growth. Thus, the aluminium rapidly penetrates the carbon wall, particularly through fissures, and forms carbide crystals which as they grow crack the carbon support.

Experiments with carbons and graphites of widely different grades and density have proved to the writer that rapid disruption of the support cannot be

prevented by mere choice of material. Metal oxide refractories such as alumina and beryllia are not satisfactory because the aluminium can diffuse through the oxide structure. Also, these refractories have poor resistance to thermal shock which creates a problem when the source is to be raised to temperature in a short period of time. A full account of the attempts made to use the foregoing materials for evaporating aluminium has been given by the writer in a previous publication[1].

The Properties of Refractory Carbides

After much fruitless work to produce a vapour source based on the above materials, a group of compounds was discovered which was highly resistant to molten aluminium.[2] The compounds were refractory carbides based on the transition elements of groups 1VA, VA, V1A of the periodic table; the properties of sintered compacts of these carbides are discussed in the treatise on hard metals by Schwarzkopf and Kieffer.[16] This discovery arose from the testing of a sample of sintered silicon carbide free from either silica or silicon impregnants which occur in commercial heater elements. It was found that pure silicon carbide was more resistant to attack by molten aluminium than tungsten or carbon. The porous nature of the sintered silicon carbide allowed aluminium to flow through it and, thus, it could not be used in normal crucible form. If a piece of silicon carbide, previously used for evaporating aluminium, was heated by a blow lamp then aluminium flowed from the interior of the body forming small metal globules on its surface.

Shortly after this discovery it was found that aluminium films evaporated from silicon carbide crucibles were slightly yellow tinted and not white as would be expected of pure aluminium. Chemical tests showed the presence of aluminium carbide in the vapour source and it was apparent that the aluminium deposit was contaminated by silicon which had been released by a reaction between the aluminium and silicon carbide. The formation of aluminium carbide was also obvious from the behaviour of the used silicon carbide when exposed to the atmosphere. There was a strong smell of acetylene and the material gradually crumbled into a grey powder as the aluminium carbide reacted with the water vapour in the air. The addition of boron carbide to the silicon carbide prevented the discoloration of the aluminium deposit[3]. Subsequent to this work a German patent by Fischer[5] appeared in which the use of silicon carbide for evaporating aluminium was described. His assertions, however, that aluminium deposited from silicon carbide is pure and that one can use carbon with a silicon carbide liner to protect the carbon, are incorrect for the reasons given above and referred to, again, later in this report. In this connection reference should be made to a patent[19] of French origin where it is claimed that silicon carbide and silicon nitride can be used inside vacuum furnaces for supporting liquid aluminium, but it is admitted that some decomposition of the silicon carbide occurs.

The range of experiments was then extended and it was found that other carbides existed which did not give rise to film contamination and whose resistance to molten aluminium was greater than that of silicon carbide. Tests were first made using tungsten carbide compounded with cobalt binders. The results were not very satisfactory because the aluminium alloyed with the cobalt so that the support swelled and became misshapen. Further work was done with tungsten, titanium, zirconium, niobium and tantalum carbides free from binders. The relative lives of these different carbides when used for evaporating aluminium in a vapour source of novel design is discussed further on.

Carbide Surface Skins. During early work on carbon crucibles tests were made to find whether the life of a container could be increased by forming a carbide skin on its surface. Silicon and titanium in powdered form were dusted over the interior of crucibles which were heated to produce a chemical reaction. In neither case did the surface layer prove effective because it was not impervious to the passage of molten aluminium. A carbon trough with a coating of silicon carbide several millimetres thick on its inside surface was also readily attacked. Silicon carbide liners inserted into carbon containers, too, proved ineffective and made it more difficult to raise the interior of the crucible to the evaporation temperature.

When the silicon carbide was raised to an elevated temperature in a carbon heater, the decomposition products were washed out of the silicon carbide by the aluminium and flowed on to the carbon, where they reacted with the heater and aluminium to form complex carbides. The heavy deposit formed sometimes protected the heater for long periods, but more often reacted so violently with the carbon that it disintegrated.

The idea of using protective carbide coatings on metal heaters for general evaporation purposes is not new. For instance, Richter[16] attempted to improve the life of a tantalum heater, used for evaporating silicon and nickel, by forming tantalum carbide on its outer surface. Metal spirals with

carbide outer surfaces, formed by heating the spiral in a hydrocarbon atmosphere, are extremely brittle and easily broken. The writer has not had any success either with this type of protected filament* or with one prepared by sintering carbide powders on its surface. This is because cracks in the outer protective layers are always present so that the life of the heater is that of its weakest point.

carbon rod which dipped in aluminium and served as a wick element. The carbon surface was treated to form a carbide or nitride skin.

Clough *et al.*[10] claimed the use of titanium, zirconium, hafnium, vanadium, niobium and tantalum metals as carbide skins, and proposed that the metal forming carbide could be added to the aluminium melt. Schuler[14] also suggested adding

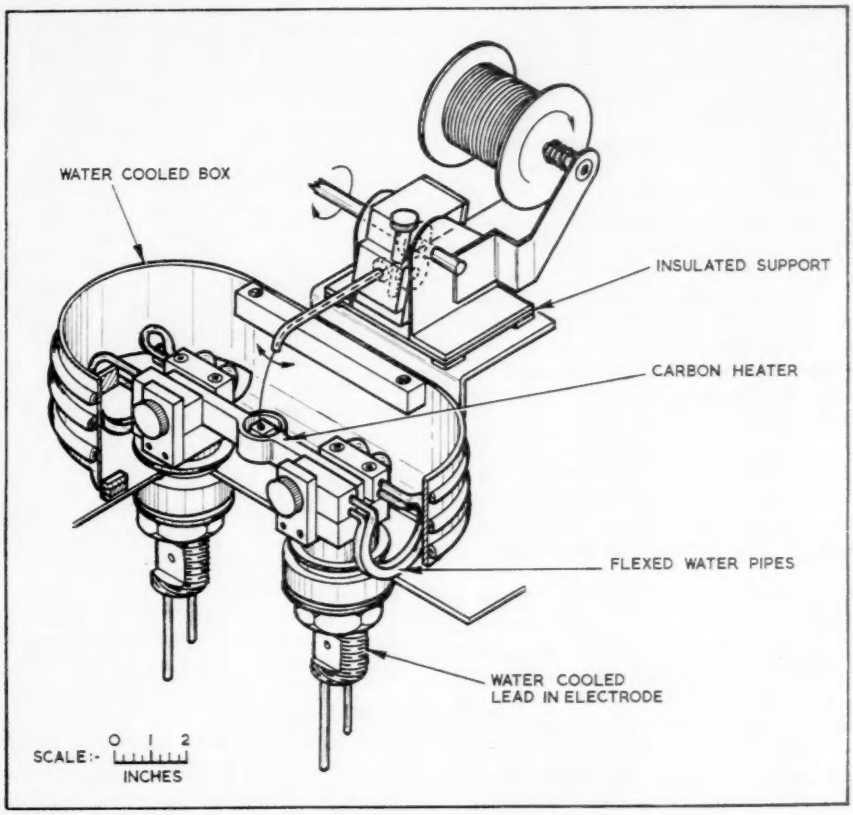

Fig. 1 General arrangement of aluminium vapour source with refractory plug and carbon bar heater.

After the writer had discontinued his attempt to use carbide protective layers several patents appeared claiming their application. Thus, it was proposed[7,8] to treat a carbon crucible with zirconia to form a zirconium carbide skin. Godley[11] and Clough *et al.*[12] claimed the use of both carbide and nitride skins. Clough *et al.*[13] stated that a carbon heater could be treated with an oxide to form a protective carbide skin. Finally Godley *et al.*[23] claimed that aluminium could be evaporated from a

the carbide forming metal to the aluminium and Alexander *et al.*[9,22] claimed that there should be an excess of the carbide forming metal on the surface of the carbon. Apparently the aim of these workers was to have metal available for healing cracks formed in the carbide layer.

The writer has found that it is difficult to maintain an excess of carbide forming metal on the carbon surface, because the metal is dissolved in the aluminium and washed away from those regions of the support where the aluminium concentration is greatest. Undoubtedly, the authors of the foregoing

* Kindly supplied by Mr. R. Titterington of Murex Ltd.

patents witnessed some improvements in the lives of carbon crucibles when using the techniques suggested, but the improvement in crucible life would not be predictable, because it is not possible to prepare carbide coatings which are completely impervious to aluminium. The penetration of the liquid aluminium is normally hastened by the carbide coating cracking under thermal shock.

Vapour Source Design

Before the chemical resistance of the refractory carbides was discovered attempts were made by the writer to produce a vapour source using electron bombardment heating[21]. The source was arranged so that the electron beam impinged directly on the aluminium surface, but trouble was soon experienced because the aluminium reacted with the support. At a later stage a source was constructed with a carbide anode on to which the aluminium was fed. This source was not suitable for the continuous coating of plastic foils because the organic materials were decomposed in the ionised gas which was formed when the electron beam was operated at a gas pressure of about 0.1-0.5 micron Hg. For these reasons an attempt was made to use the carbide materials with more conventional forms of heating.

Most of the refractory carbide materials are expensive and their fabrication into sintered components is costly. Thus, at present it is not economically possible to make either a large crucible or a combined crucible and heating element from a refractory carbide.

All of the refractory carbides suffer to different degrees from attack by molten aluminium and crazing due to thermal shock. Thus, if the vapour source consists of a single element, *e.g.* a resistance-heated trough, its performance as a heating element is impaired long before the refractory material has ceased to be a satisfactory support for the evaporant. Therefore, it is better to make the source in two parts and separate the evaporator from the heater. Further, if the aluminium is fed on to the refractory material, an expensively shaped crucible is not required. A number of other advantages accrue from this arrangement, *viz.*

(i) the evaporator can be in the form of a thick plate so that ample carbide material exists for resisting attack, and

(ii) the heat energy lost by radiation is less than that from a large crucible holding the complete aluminium charge.

An evaporation source designed on this principle will now be described.

The Plug Evaporator

The most convenient and cheap material available for the fabrication of a heating element is carbon, but it is essential that the liquid aluminium does not contact its surface. After many experiments using carbon heaters the successful evaporator produced had the form shown in Fig. 1. The vapour source consisted initially of a cylindrical refractory plug inside a cavity in a carbon bar heater. The plug was of smaller diameter than the cavity in the heater so that liquid aluminium could not easily flow from the plug on to the carbon. Aluminium wire from a stock reel was fed on to the heated plug, where it melted and flowed over the surface and evaporated. Any metal flowing down the vertical sides of the cylinder evaporated before reaching the carbon at the base of the plug. Vapour atoms which were emitted in the cavity and collided with the heater were re-evaporated back into the main vapour stream without chemically reacting with the heated carbon. Liquid metal could be prevented from reaching the base of the cavity and reacting with the carbon heater by controlling the feed rate of the aluminium wire, the depth of the refractory cylinder and the evaporation temperature. The early plugs rested on three small projections so that molten aluminium could not bridge the gap between plug and heater. However, by limiting the rate of wire feed, the metal could be evaporated before reaching the base of the plug. The whole surface of the plug base could then rest on the carbon heater, thereby improving the heat transfer.

A further improvement, suggested by Barker,[15] an associate of the writer's, was to make the carbide plug of cubic shape as actually shown in Fig. 1. Then, as the uppermost surface of the plug became eroded with use, it was possible to turn the plug to expose a new face and thus use the carbide material to the maximum effect.

Heating Elements. In early models the electrical connections to the heater were made by clamping water-cooled copper terminals to the upper and lower surfaces of the carbon. When the heater was raised in temperature or cooled, there was a tendency for it to bow downwards or upwards and impose a stress on the carbon which was not released, because the terminals only permitted the heating element to expand and contract longitudinally. The connections were re-designed as shown in Fig. 1, to clamp the carbon heater on the vertical sides, so that if bowing occurred, the stress could be relieved by the carbon sliding in the holder. Only longitudinal expansion and contraction occurs

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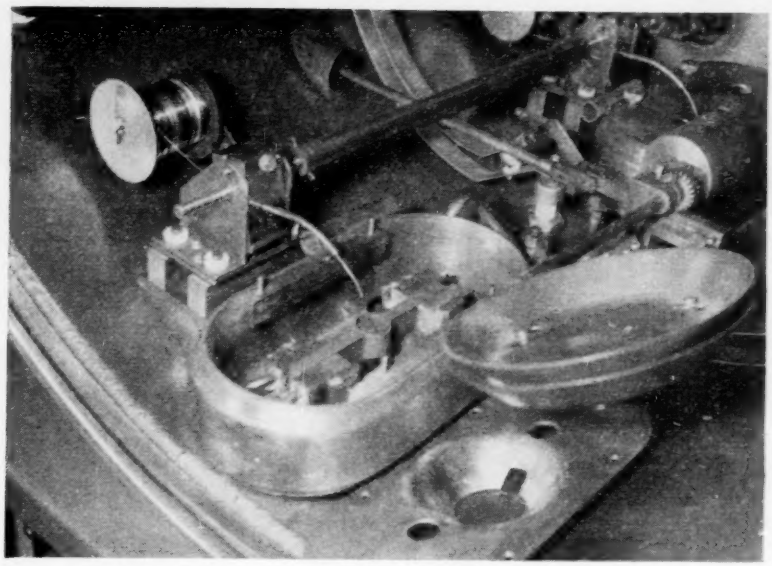


Fig. 2 General view of vapour source. The lid of the water-cooled radiation shield has been removed and is resting in the foreground. The vapour shutter is also open.

Fig. 3 Method of using refractory plug with carbon susceptor and high frequency heating.

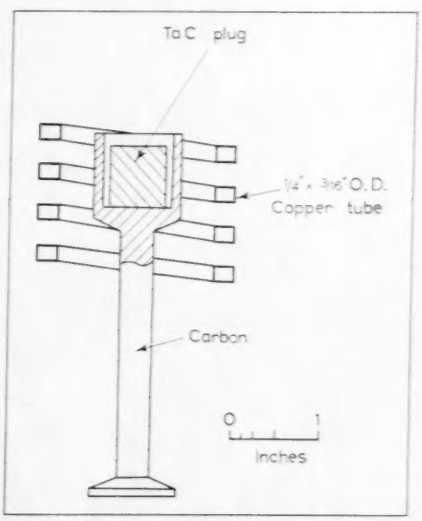
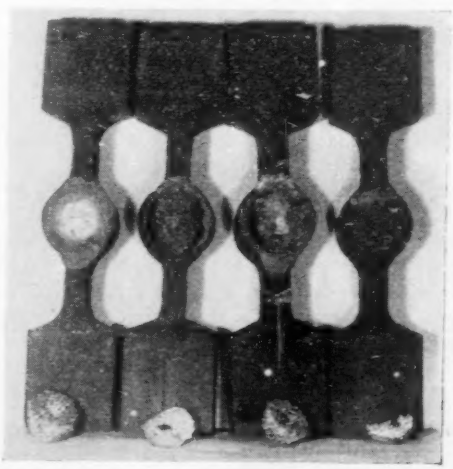


Fig. 4 Attack of carbon heater due to decomposition products from reaction between aluminium and silicon carbide flowing into heater cavity.



in the horizontal plane because in this plane the heater is symmetrical about its axis. Good electrical connections were facilitated by clamping directly on the carbon surface; copper electro-plating the ends of the carbon heater as is practised by some workers was not found necessary. The terminals clamping the heater were held in position by flexing the copper cooling pipes, see Fig. 1, and it was only necessary to tighten the thumb screw until it met slight resistance. Elaborate connections such as the electro-magnetic clamps used by Alexander *et al.*[20] were not required.

The heating element illustrated in Fig. 1, can be operated from a low tension supply giving a variable voltage output of 0-15 V at 1,000 A. A power input of 11 kW is used with an applied voltage of the order of 11 V when evaporating between 2-4 g./min. of aluminium. Some 50% of this power input is lost as heat to the cooled electrodes* and some 3.5-7% (equivalent to 0.35-0.7 kW) as latent heat of evaporation; the remaining heat is dissipated as heat radiation. To prevent undue heating of the target the heating element is surrounded by a water-cooled box made of copper. The lid of the box is heavy gauge copper sheet which is cooled by conduction to copper bars clamped to the vertical sides of the box. The absence of water-cooling connections to the lid simplifies its removal when the heater requires replacement as is shown in Fig. 2.

Wire Feed. Aluminium wire from a stock reel is passed between two hardened knurled wheels which are coupled by a pair of gears and driven so that they push the wire down a guide tube on to the evaporator. It was found by Mr. Barker that when only one of the knurled wheels was driven the feed wire jammed, whenever there was a kink in the wire, but this did not arise when both wheels were driven. The spacing between the knurled wheels can be adjusted by raising or lowering the shaft of the driven wheel.

With this system the force between the knurled wheels can be sufficient to convert the aluminium wire into a ribbon, but for the feeding purposes this is not necessary. However, it is useful if the knurled wheels heavily indent the aluminium because the indentations prevent rapid melting back of the wire, when its leading edge is exposed to heat radiation from the top of the refractory plug. Should a molten globule of metal begin to form it cannot easily bridge the thinned sections at the indentations. Also, for this reason, the wire is fed on to the plug in rapid pulses because a slow rate of wire feed may result in the periodic formation of globules which fall and flood the source.

It is common practice to ground one end of a heating element and, if the wire feeder is also grounded, there will be a potential difference between the centre of the heater bar and the feed wire. Thus, when the feed wire touches the plug, arcing will occur. To prevent this the feeder is electrically isolated from the heater by mounting it on low-voltage insulators.

H. F. Heating. The refractory plugs described here can be raised to the evaporating temperature by high frequency induction heating. Using a 7 kW h.f. set with a frequency of 500 kc/s. a sintered TaC cube of 14 mm. edge could be raised to 1,500°C and higher without difficulty, but, if aluminium had been fed on the plug for a long period, a deposit would have rapidly built up on the h.f. coil. To avoid this, the plug was raised to temperature surrounded by a carbon shield, as shown in Fig. 3. Both the carbon and refractory plug were heated by h.f. induction. The carbon shield served as a vapour reflector and kept the h.f. coil free from deposits. The leads connecting the coil to the generator were kept short to avoid undue losses and were about 12 inch. long.

If a power supply of low frequency is used such as a motor generating set giving 5-10 kc/s., then the carbon vapour reflector is essential as a susceptor.

Using the high-frequency generator described above the carbon shield and plug shown in Fig. 4 can be held at 1,500°C with a power input of 2.5 kW. Undoubtedly, the power requirements are greatly reduced when there are no heat losses to massive cooled electrodes as experienced with a carbon resistance heater.

Radiation Losses. The outer surface area of the carbon susceptor and the plane area of the cavity are equal to 29 cm^2, whereas the surface area of the carbon resistance heater described above is 53 cm^2. The greater area of the resistor increased the heat lost by radiation, which from measurements was 5.7 kW compared with 2.5 using h.f. heating. The heat energy radiated per second can be calculated from the electrical power lost and the values obtained for both sources were of a comparable order, being 23 and 28 cal./$cm.^2$./sec. for the h.f. and resistance sources respectively. Allowing for the emissivity of carbon being about 0.89, the corresponding temperatures of each source can be found. They are 1,720 and 1,850°C respectively. This is higher in each case than the temperature measured with an optical pyrometer focused on the refractory

* This produces a temperature rise of 9.75°C in the cooling water passing through one electrode at a flow rate of 4 l./min.

Table 1. Useful Lives of Some Refractory Carbides Compared with that of Pure Tungsten when Used for Evaporating Aluminium.

*Refractory Materials**	*Chemical Formula*	*Heat of Formation* $-H_{298}$ *k.cal/mole*	*Useful Source Life† hours*	*Remarks‡*
Tungsten	W	—	0.2-0.6	W dissolved in the Al and deposited on the carbon heater
Tungsten Carbide ('Elmarid' with Cobalt binder)	WC+4½% Co W_2C+Co	— —	1.5 1.0	Al dissolves the cobalt and plug swells, plug material deposited on carbon heater
Tungsten Carbide (binderless)	WC	8.4±3.0[17]	3.5	Life determined by erosion
Tantalum Carbide	TaC	9.0±7.0[17] estimated	4.0 7(cube)	Life determined by erosion
Niobium Carbide	NbC	—	1 (cube)	Destroyed by erosion
Titanium Carbide	TiC	57±10[17]	0.2-2.5	Usually cracks during first few mins. of evaporation
Zirconium Carbide	ZrC	40±10[17]	0.2-2.5	Longest life is for exceptional plugs.
Silicon Carbide	SiC	28±3.0	0.5-0.75	Reacts with liquid Al and free Si evaporated. Decomposition products react with heater.
Silicon Carbide +Boron Carbide	SiC+$B_{27}C_5$	—	0.5-1	$B_{27}C_5$ added to prevent Si evaporating. Decomposition products react with carbon heater.
Aluminium Carbide	Al_4C_3	44±6[17] 21[18]	—	Reaction product formed when molten Al contacts the carbon heater

*The source material was either a cylinder of approx. 19 mm. diameter × 12.7 mm. length or a cube of 14 mm. edge.
† Aluminium wire 20 s.w.g. fed on to plug at 65 injections/min. in lengths of 11/16 inch.
‡ The plug material was raised to 1,500°C from room temperature in about 3 minutes.

plug, which was 1,500°C. The temperature difference probably arose from the emissivity of the TaC-plug being low, *e.g.* at an observed temperature of 1,500°C the reading could be 200°C less than the true value if the emissivity was equal to 0.3.

Performance Characteristics of Carbide Materials

A range of refractory materials in the form of cylinders and cubes have been used in the resistance heated evaporator shown in Fig. 1 and their useful lives are given in Table I. The results are averages for between five and ten plugs of each material quoted. The life of each material was normally terminated by the evaporating base disintegrating and aluminium flowing on to the carbon heater.

The refractory plug was operated at about 1,500°C (optical pyrometer) with aluminium wire of 20 s.w.g. fed on to the plug surface at a rate of 65 impulses per minute and an injection length of 11/16 inch per impulse. Thus, in one minute 44 inches of wire were evaporated equivalent to a mass of 2.01 g. *Decomposition Products.* As explained in an earlier section silicon carbide reacts with aluminium, thereby liberating volatile silicon. When this occurred, decomposition products were washed out of the plug into the cavity where they reacted with the carbon heater. These reaction products formed a complex carbide on the heater surface with the plug cemented in its centre. The complex coating on the carbon sometimes protected it against further attack and when this occurred the useful life of the source was about 45 min. However, the carbon

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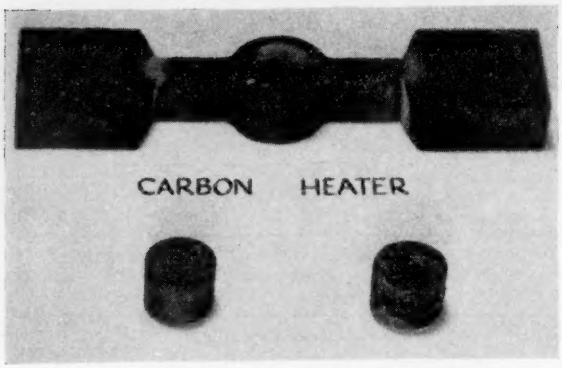
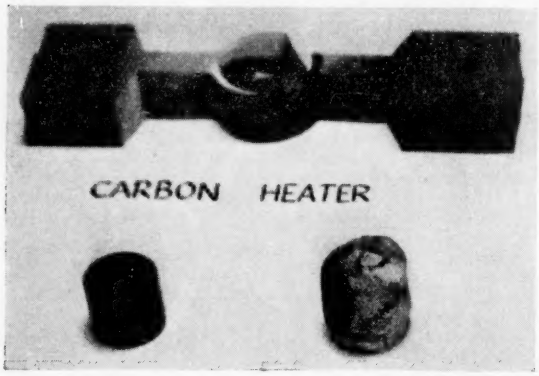


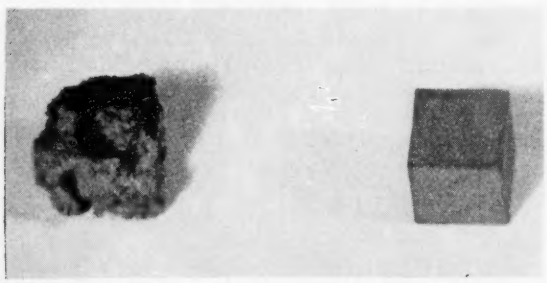
(1) (2)

Fig. 5 Alloying reaction of aluminium with the cobalt in bonded tungsten carbide (see Fig. 5b below) compared with the inertness of binderless tungsten carbide (see Fig. 5a above).
(1) Plug prior to use. (2) plug after 30 mins. use (above) and a few mins. use (below).



(1) (2)

Fig. 6 Comparison of used and unused tantalum carbide plugs. Period of usage; $4\frac{1}{2}$ hours.



invariably broke in the early stages of evaporation due to localised reaction with the decomposition products. The appearance of a group of carbon heaters after prolonged use with silicon carbide are shown in Fig. 4. Reaction between the decomposition products and the carbon heater still occurred, when boron carbide ($B_{27}C_5$) was added to the silicon carbide to prevent evaporation of free silicon[4].

Reaction between the carbon and the materials washed out of the refractory plug was also observed for tungsten carbide containing a cobalt binder, such as is normally used for cutting tools. However, the source life was greatly increased when the plug was made from binderless tungsten carbide, because (i) the plug material held together better during evaporation, and (ii) the carbon support was not attacked because decomposition products were almost absent. The difference in the appearance of the pure and bonded grade of tungsten carbide can be seen in Fig. 5.

Thermal Shock. With binderless refractory carbides the cavity in the carbon heater remains clean throughout the life of the plug, providing the pure carbide does not disintegrate and permit molten aluminium to flow on to the heater. Carbides of titanium and zirconium are particularly prone to crack during initial heating or in the early stages of evaporation. Observation of the source material suggests that these carbides are more readily attacked than tantalum carbide but are more resistant than tungsten carbide. However, their maximum life cannot be obtained because they crack under thermal shock.

Evaporation rates of 2.01 g./min. for as long as seven hours have been achieved with tantalum carbide cubes of 14 mm. edge. The plugs are continually turned to expose a new face for wear, so that the erosion is not confined to one surface. The effect on a tantalum carbide plug used in this way for $4\frac{1}{2}$ hours is shown in Fig. 6. During seven hours evaporation from a single vapour source, some eight miles of roll material 12 inch. wide can be coated with aluminium with a thickness of about 0.04 microns, *i.e.* with some 50% of the evaporated metal being lost to the chamber walls. These figures are for a source-receiver distance of 11 inch. with the receiver moving at a speed of 100 ft./min. Obviously proportionally greater outputs can be obtained by increasing the number of sources.

The life of a refractory carbide plug depends not only on the period of exposure to aluminium but also the number of times it is heated and cooled because this promotes cracking of the material.

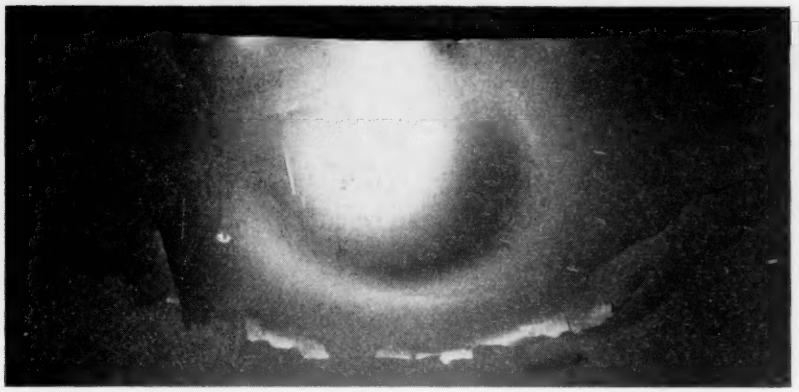


Fig. 7 Aluminium deposit about 10/1000 inch thick peeled from a partially polished metal plate arranged at a normal distance of 11 inch. from the source. The central area of the deposit reproduces on its outer surface the fine structure of the metal receiver surface. The reflected image is that of an incandescent lamp. At vapour incidence angles above 45° the substrate surface detail is obliterated by granular growth in the deposit.

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Vapour Intensity Distribution

The distribution of the vapour intensity from the evaporation source shown in Fig. 1 has been measured by condensing the aluminium on a stationary receiver at a normal distance of 11 inch. from the source. Coatings some 10/1,000 inch thick, formed after 45 minutes evaporation, have the appearance shown in Fig. 7. The central region of the deposit reproduces the small surface imperfections in the rolled steel sheet used for the target and the vague outline of the image of an incandescent

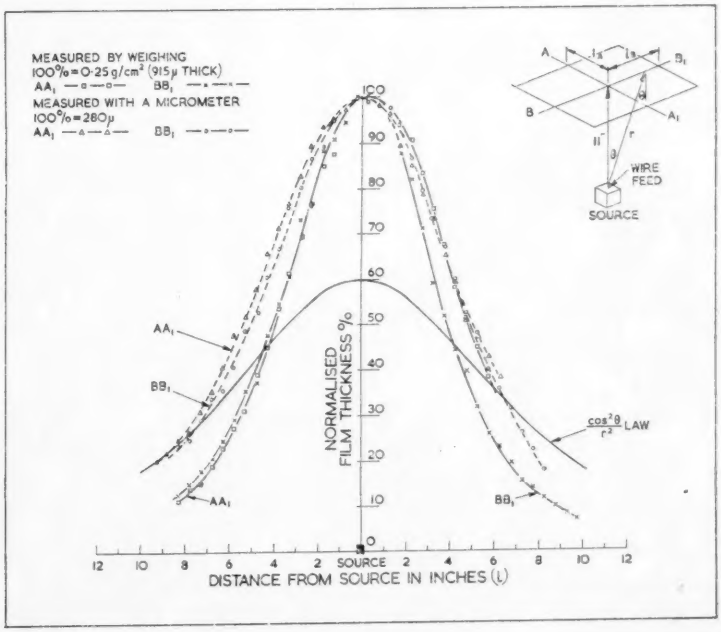

Fig. 8 Distribution of evaporated aluminium on a stationary receiver arranged at a normal distance of 11 inch from the aluminium vapour source. Theoretical curve is the $\cos^2\theta/r^2$ relation for a surface source.

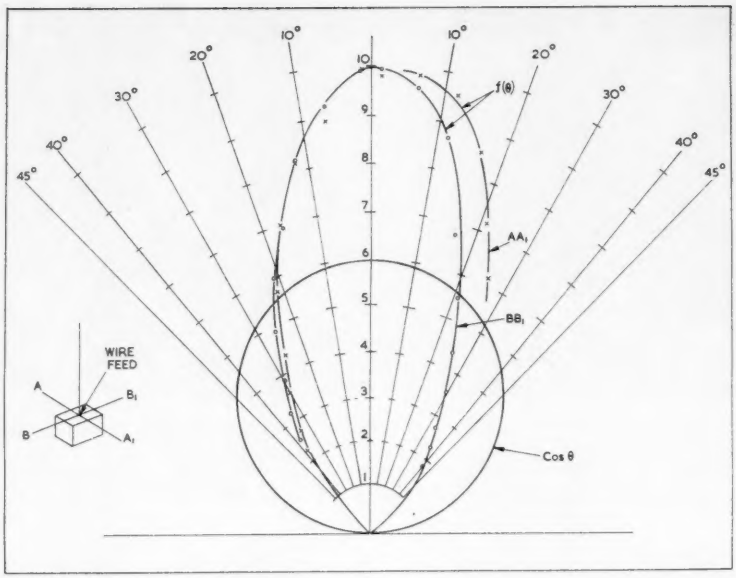

Fig. 9 Polar diagram of the vapour intensity.

lamp can be seen reflected in the central region. Surface detail in the outer deposit has been obliterated by a granular structure in the coating. The formation of the matt surface is due to the mode of film growth, *i.e.* vapour atoms incident at angles above 45° are unable to penetrate the grain interstices and are preferentially deposited on surface prominences and projecting grains, as shown by Holland[1]. It is of some novelty that with a deposit obtained after prolonged evaporation it is possible to see the grain growth without the aid of a microscope.

Measurement of the source intensity distribution is likewise rendered easy by the greater mass of the deposit. Thus, plotted in Fig. 8 is the film distribution determined by both weighing and measurement of thickness using a micrometer. The micrometer and weighing measurements agreed within 5%, assuming the deposit had bulk density. Also, plotted in Fig. 8 is the film distribution assuming that the evaporator emits in accordance with Knudsen's cosine law, *i.e.* the mass per unit area m condensed is given by:—

$$m = \frac{M \cos\theta \cos\phi}{\pi r^2} \qquad (1)$$

where M is the mass evaporated
r the evaporation distance
θ and ϕ the angles of incidence to the normal of the evaporation surface and the receiver respectively.

If one allows in Fig. 8 for the difference in the vapour incidence angles and the evaporation distances at different points on the receiver surface, then a polar diagram of the vapour emission can be drawn. Such a diagram shows the mass of vapour passing through unit solid angle at different incident angles to the surface of the source. Thus, for a true surface source, the mass of vapour emitted in unit solid angle at an incidence angle θ to the source is given by:–

$$\frac{M \cos\theta}{\pi} = m \cdot \frac{r^2}{\cos\phi} \qquad (2)$$

and for a source, the distribution of which differs from that of the cosine law as found here:—

$$\frac{M f(\theta)}{\pi} = m \cdot \frac{r^2}{\cos\phi} \qquad (3)$$

The polar diagram in Fig. 9 was obtained from the mass distribution of the deposit on a plane receiver using Equ. 3. The curve shows that there is marked beaming and departure from a surface source. If the intensity distribution of the source had followed a cosine law, the polar diagram would have been a circle and this has been calculated from the total mass evaporated and plotted in Fig. 9 in

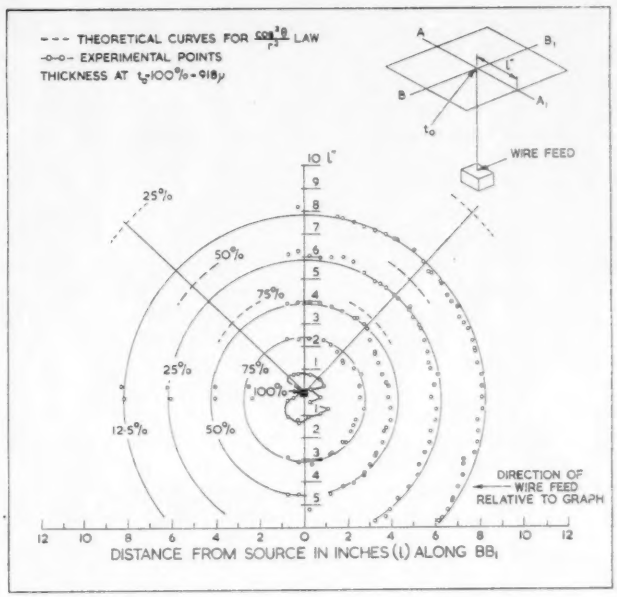

Fig. 10 Lines of constant surface density (m/A) on a receiver 11 inch. above the vapour source.

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normalised form. The intensity values of the actual source have also been normalised so that the curve is for $f(\theta)$. By comparing the ideal and measured curves it is possible to see how the beaming effect increases the vapour intensity at normal incidence to the source and reduces it at high incidence angles.

The beaming effect may also be seen in Fig. 8 where both mass and thickness measurements are compared with the curve for an ideal surface source. The difference between the two experimental curves in Fig. 8 is greater than the error between the methods of measurement and the results imply that

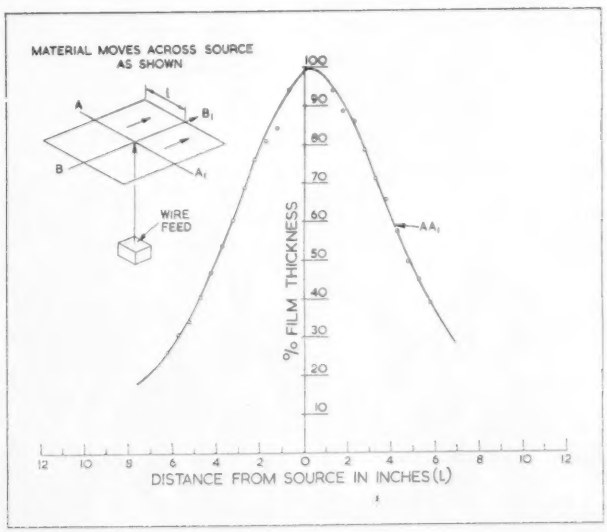

Fig. 11 Curve shows final film thickness distribution across receiver after summing the total metal deposited at right angles to the distribution curve.

The result is equivalent to that obtained when an element of a plane receiver traverses the vapour beam as shown in the diagram.

there is progressive departure from the cosine law as evaporation proceeds. Thus, the curve nearest to the ideal law was measured after 50 minutes evaporation and that showing greatest beaming after 3 hours evaporation. Beaming of the vapour atoms arises from the emission of vapour from the cavity surrounding the plug and as evaporation continues a cavity may be worn in the plug which increases the beaming effect.

A large area of a deposit on a plane receiver was cut into squares and weighed and the lines of constant surface density (m/A) are plotted in Fig. 10. The values obtained assuming a surface source are shown in the dashed curves. If one sums the masses deposited at right angles to a line drawn across the receiver a distribution curve is obtained as in Fig. 11. which is similar to that produced on an element of a receiver traversing the vapour beam, *e.g.* a continuously moving plastic foil. The preferred evaporation characteristics of the vapour source reduce the amount of metal vapour lost at the edges when coating plane surfaces. Uniform deposits can be obtained by using a bank of such sources placed at right angles to the direction of the moving web.

My thanks are due to Mr. A. Hilliard and Dr. J. Parisot of the Société le Carbone Lorraine for the assistance they have given in the production of different types of refractory materials, to Messrs. N. Sutherland, B. J. Williams and D. Barker for the help they have rendered in the testing and development of the vapour source, and to Mr. A. S. D. Barrett, Technical Director of Edwards High Vacuum Ltd., for permission to publish this report.

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The publishers endeavour to make the compilation of abstracts published in this section as comprehensive as possible, but cannot undertake to trace and quote all relevant information published on these subjects.

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10 — VACUUM ENGINEERING (GENERAL) — 10

Vacuum Education in the United States — 1/I

United States. Training in vacuum technology in the U.S.A. is discussed, taking into consideration universities, industries using vacuum processes, vacuum equipment manufacturers, industrial research laboratories, Atomic Energy Commission installations and laboratories operated by the U.S. Government. The most wide-spread method of training is of the on-the-job variety, involving working with vacuum equipment and with more experienced personnel, the use of informal conferences and the use of the technical literature. Complete courses of instruction in vacuum technology, in universities or industry, are quite rare. The formation of the Committee on Vacuum Techniques, Inc., is discussed briefly. It is expected that vacuum processes will be used more and more widely in the future. However, it is believed that the on-the-job type of training will still remain the basic method. It is very unlikely that courses in vacuum technology will be offered in the regular university curricula. The trend will probably be toward the introduction of such courses in university extension systems.

(Author)

Article by A. Guthrie *Vacuum* 5, October 1955 5-24

Vacuum Technique — 2/I

France. Tables, extending over 4 pages, give data of the mechanical rotary and oil diffusion pumps produced by the leading vacuum equipment manufacturers in France, United States, Great Britain, Germany, Italy, Switzerland and Liechtenstein. The data refers to the number of stages, speeds, ultimate pressures obtainable, power consumption, etc. It follows information of interest to the design engineer concerned with the construction of complete vacuum installations and, finally, a discussion is added on suitable pumping fluids, joints, stopcocks, valves and seals.

Article by R. Doré, *Ingen. Tech.* September 1956 79-89

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Mechanical Vacuum Pumps — 3/I

See Abstract No.: 2/II

Vapour Pumping Characteristics of Gas Ballast Pumps — 4/I

United Kingdom. The mechanism of contamination when vapours are pumped by oil-sealed rotary pumps is described and a method is discussed for calculating the degree of protection afforded by gas ballast in terms of the maximum mass flow rate at which oil-insoluble vapours can be pumped without significant condensation of vapour in the pump. It is shown experimentally that, though this calculated maximum flow rate does correspond approximately to the practical limit for no condensation, it can often be greatly exceeded without cumulative contamination or serious impairment of pump performance. The somewhat different characteristics when pumping oil-soluble vapours are discussed and illustrated by experimental results, and it is concluded that, although gas ballast can generally provide considerable protection in such cases, a high proportion of the volumetric and mass pumping rates theoretically possible on the basis of pump displacement is more likely to be achieved in larger and hotter-running than in smaller and cooler-running pumps.

Article by B. D. Power & R. A. Kenna *Vacuum* 5, October 1955 35-58

Vapour and Molecular Pumps — 5/I

Germany. Diffusion pumps, vapour booster pumps, the molecular pump, the ion-pump and methods of reducing the gas pressure in the vessel sealed off after pumping are discussed. The special features distinguishing the operating principle of the vapour-booster pump and that of the diffusion pump are described in detail. Generally, the diffusion pumps have their highest pumping speeds in the pressure range below 10^{-3} mm. Hg and the vapour booster pumps are designed to give the highest speeds at the level of about 10^{-1} mm. Hg. The comparative merits of various pump fluids such as mercury and tetrachlordiphenyl are considered. Backstreaming of the pump fluid can be reduced to a minimum by suitable means. In some cases, for instance in vacuum impregnation, contamination of the impregnating material can be avoided by operating the diffusion pump with the impregnating material itself as the pump fluid. The molecular pump, first proposed by Gaede in 1909, is a mechanical pump. Operating with a backing pressure of 0.1 mm. Hg, it may reach an ultimate of 10^{-6} mm. Hg and has a speed of 8 litre per second at a pressure of 10^{-3} mm. Hg. Due to the operating principle of the pump the problem of backstreaming of contaminating vapours is absent. The pump is employed for the evacuation of cathode-ray oscilloscopes and electron microscopes. The latest type of pump is the ion-pump where the gases to be pumped are ionised and the ions collecting in the cathode space are removed by means of a diffusion pump. This type of pump, too, produces a 'clean' vacuum. It reaches ultimates of 10^{-11} mm. Hg and its speed is comparable to that of diffusion pumps. Its disadvantage is a high power consumption. The article concludes with remarks on the gettering process applied when the evacuated vessel has been sealed off, and the description of a method of measuring the speed of vacuum pumps generally.

Article by P. Hochhäusler *Elektrotech. Z.* 27, 21.11.1955 417-423

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6/I

Diffusion Pump with Freon-12

France. The conventional diffusion pumps working with oil or mercury as the pump fluid operate on the principle of the 'hot cycle' where the vapours of the fluid are at elevated temperatures and are condensed at ambient temperature. The authors describe a pump, proposed to operate on an analogous 'cold cycle' employing a fluid which is available in vapour form at ambient temperature and which is condensed at very low temperatures. The two designs discussed in the article employ Freon-12 (dichlorodifluoromethane). This pump fluid which is virtually inert at temperatures below 200°C, has a boiling point at atmospheric pressure of −29°C and solidifies at −158°C. Its vapour pressure at ambient temperatures is 4 atmospheres. In one design Freon vapour is admitted through a needle valve from a normal, commercially available, Freon bottle to a cylindrical container, the lower end of which is submerged in a Dewar holding liquid nitrogen, and the upper end of which is connected to the recipient to be pumped. Pumping action is instantaneous and after a few moments a pressure of 10^{-5} mm. Hg is obtained in the recipient. The pumping speed in the range of 10^{-5} to 10^{-3} mm. Hg is approximately 35 litres per second. The consumption of Freon is stated to be 1 litre in 9 hours pumping time. A method of circulating the Freon employed in the pump in a closed circuit is described.

Article by J. Delcher, R. Geller, G. Mongodin & F. Prevot *Le Vide* 11, March-April 1956 78-80

7/I

Electrical Clean-Up of Gases

United States. The mechanism by which the Bayard-Alpert ionisation gauge pumps helium has been the subject of recent studies (L. J. Varnerin, Jr. and J. H. Carmichael, *J. Appl. Phys*, 26, 782 (1955)). It has been shown that the gas is trapped in the thin film of sputtered metal which is deposited on the glass walls of the tube. In this report, a phenomentological theory of pumping is presented. The theory is compared with experiment.

Report by L. J. Varnerin Jr. & J. H. Carmichael *U.S. Dept. Air Force Rep.* 71F191-R6 October 1955

8/I

Use of Krypton-85 in Measuring Gas Clean-Up Rates

United Kingdom. An important factor in the operation of pre-T. R. valves is the clean-up of the rare gas filling. The rate of the clean-up can be measured with the help of radioactive krypton, Kr-85, its half-life being 10 years and its radiation mainly beta (680 keV) and some gamma (500 keV). Two measuring techniques have been used: (*a*) The collimated beta radiation from a section of the valve remote from the discharge and gas clean-up region is monitored during the life of the valve, by Geiger counter. The activity then measured is due to free gas only and the count-rate is proportional to the free gas density. (*b*) For low clean-up rates, the total activity of the valve is measured after a known period of life, before and after opening the valve to atmosphere. The residual activity then corresponds to the gas clean-up into the valve walls. An example is given of technique (a) used for a silica tube pre-T.R. crossing two wave-guides, and containing 7 mm. Hg of krypton. The ratio of final to initial pressure is shown in a graph, and the areas over which clean-up occurred in a test run of 250 hours are indicated.

Letter by D. J. Harris & P. O. Hawkins *Nature* 177, 11.2.1956 285-286

9/I

Origin and Analysis of Gas in Electron Tubes

See Abstract No.: 43/IV

10/I

Gettering of Gas by Titanium

United States. The gettering properties of titanium have been studied for a number of gases, to evaluate the metal for vacuum-tube use. The titanium, in the form of 1.5 inch diameter rings, 0.005 inch thick and $\frac{1}{4}$ inch wide, was contained in a special Pyrex getter bulb connected to a vacuum system and gas supply. The titanium was cleaned by degreasing with acetone, etching in hot hydrochloric acid, and washing with distilled water. This produced a mat finish. The gain in weight of the metal and change in pressure of the system, the volume of which was known, enabled the amount of gas sorbed to be determined. The system was first baked at 450°C for one hour. The metal ring was then heated to 1,150°C for ten minutes until the pressure was less than 10^{-3} micron Hg. During this process, the metal dissolved the surface contamination caused by O_2, N_2, carbon etc., and also released hydrogen gas. Mass spectrograph analysis has shown the latter to be the principal gas evolved by hot titanium. The gas to be gettered was then released into the system and pressure-temperature-time characteristics determined. N_2, Co_2, O_2 and air were all gettered by hot titanium in the range 700–1,100°C. With N_2, Co_2 and oxygen in small concentration the pressure decreased almost linearly with time. A surface-barrier-limited sorption is postulated to account for the constant rate of combination. The logarithm of the rate of N_2 sorption *vs.* reciprocal temperature gave a plot of two straight lines. The break point observed at 900–1,000°C corresponds to a phase change in the metal. With oxygen the sorption rate falls when the sorbed gas reaches 100 μl/cm^2 at 700°C. This seems to indicate a diffusion barrier action. X-ray data showed TiN, TiO, and TiC to be present when nitrogen and CO_2 had been sorbed. Hydrogen sorption was also studied. This gas is gettered readily at 25–400°C. Failure of some workers to observe such sorption may have been due to the presence of a surface oxide layer on the getter. Successful vacuum tube gettering by titanium necessitates operation at high and low temperatures (sorption and release). A summary of the rules of sorption observed is given in a table, reproduced on the next page.

Article by V. L. Stout & M. D. Gibbons *J. Appl. Phys.* 26, Dec. 1955 1488-1492

I — General Science and Engineering — I
Contd.

Abstract No. and References

Gettering Properties of Titanium

	Temp°C	*Nitrogen*	*Oxygen*	*Carbon dioxide*	*Air*
Gettering rate (μl/cm² min) at various temperatures	700	0.4	11	0.15	
	800	0.9	127	1.7	
	900	2.0	*	3.9	
	1000	5.0	*	15	
	1100	2.0	*	48	
Residual gases after gettering	Relative quantity	$7/10^4$	$4/10^3$		$9.8/10^3$
	Gas content	50% A, 50%Ne	90%A, 10%Ne		% A in air
Total quantity gettered in μl/mg		160	90	50	

* Too rapid to measure.

Improvements i.o.r.t. Getter Materials and Methods for Their Production

11/I

Germany. Getters available in the form of pills, manufactured from various powderised components, are known to have the disadvantage that the separate constituents of the powder tend to react with each other soon after the pill is made. The reaction products, essentially water, reduce the getter efficiency. The object of the present invention is to avoid the formation of water or other contaminants by depositing each getter component in turn in a vacuum. The material most sensitive to atmospheric influences is first deposited and this is followed by a more resistant material. By way of example, barium is deposited on an outgassed foundation such as a wire or a metallic surface and then oxygen is introduced so as to combine with the barium and produce an oxide free from water. Finally, a layer of aluminium is deposited as a protective sheath. By depositing the two components without breaking the vacuum their contact is so intimate that even when the getter is subsequently exposed to atmosphere any penetration of water or other impurities which might lead to undesirable chemical reactions is avoided. The getter unit produced as indicated above can be used in vacuum envelopes containing very sensitive surfaces, such as photo-cathodes, without causing them to deteriorate. It has been found that it is not desirable to fire the getter before the latter cathodes are formed since the activation process may counteract the effect of gettering.

W. Flechsig & Fernseh G.m.b.H. *Brit. Pat.* 738,485

Experiments at Very Low Pressures

12/I

United States. Research work carried out in the last six years and devoted to the production and measurement of pressures below 10^{-8} mm. Hg is surveyed. Reference is made to new techniques as follows: (1) An ionisation gauge to measure pressures down to 10^{-11} mm. Hg (the Bayard-Alpert gauge), which eliminates the effect of soft x-rays produced at the grid causing the release of photoelectrons at the ion collector of a conventional ionisation gauge. (2) An all-metal vacuum valve capable of high-temperature bake-out. (3) The uses of 'ion pumping' in which the ions produced in the ionisation gauge are permanently removed when they strike the negatively-charged collector. (4) Specific design features of ultra-high vacuum systems. (5) Demountable joints consisting of gold or copper gaskets clamped between stainless steel flanges. Using the various techniques in conjunction with a thorough bake-out of the whole system it is possible to obtain pressures of 10^{-10}–10^{-11} mm. Hg with comparative ease. The factors limiting the ultimate pressure to about 3×10^{-11} mm. Hg are discussed. It is shown that this is entirely due to the diffusion of atmospheric helium through the glass envelope of the system. In the absence of pumping this causes a rate of rise of pressure of the order of appr. 3×10^{-11} mm. Hg per minute; that is, a total rise of 1 micron per century. When the vacuum system was enclosed within another vacuum system it was found that the rate of rise of pressure in the inner system vanished after about 60 days. This suggested the existence of a diffusion process in the glass and it was found possible to calculate the value of the diffusion coefficient D and the solubility S from experimental observations. A subsidiary experiment on the diffusion of helium through a Pyrex disc gave values for D and S which agreed with those obtained above and confirmed that helium was the gas involved. It is believed that pressures considerably below 3×10^{-11} mm. Hg have been obtained by enclosing one vacuum system within another but there is no reliable method of measuring pressures as low as that. It has also been shown that conventional diffusion pumps are capable of producing pressures as low as 10^{-11} mm. Hg provided that the backstreaming of oil vapour is prevented by the use of a special trap consisting of the standard re-entrant glass tube with the space between the inner and outer trap packed with corrugated copper sheet. These traps were found to perform satisfactorily even when they were not refrigerated.

Article by D. Alpert *Science* **122**, 21.10.1955 729-733

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13/I

Improvements i.o.r.t. Devices for Measuring Very Low Gas Pressures

See Abstract No.: 41/II

14/I

Electromagnetically Operated Ultra-High Vacuum Valve

See Abstract No.: 93/II

15/I

A Corrosion Resistant High-Vacuum Valve for Liquids

United Kingdom. The valve described was designed to enable the study of cationic polymerisations. The objective was to admit 0.5–5.0 ml. of trifluoroacetic acid and of titanium tetrachloride in hexane into a high vacuum system with a precision of 0.02 ml. The liquid constitutes a solution which cannot be distilled, must be kept free of water and tap greases and, in addition, is highly reactive and cannot be allowed to come into contact with mercury vapour or with organic materials. The valve is of the all-metal type. It consists essentially of a cylindrical brass casting, one inch in length, with two copper-to-glass seals fixed to it, one on the axis of the cylinder and the other on a radial hole at the same end of the cylinder. The other end of the cylinder is closed off by means of a circular diaphragm of soft copper foil 0.005 inch thick stiffened by means of an annular corrugation. A length of 2 B.A. brass studding passes through a seal at the centre of the foil and is secured to an inner cylinder. A rotating handle attached to the outer end of the stud causes the foil and inner cylinder to move along the axis of the brass casting. The end socket of the movable inner cylinder carries a $\frac{1}{4}$ inch diameter ball bearing which fits into a spherical seating machined at the junction of the bores running from the two metal-glass seals. This serves to isolate the two lines. Withdrawal of the ball bearing connects the two pipelines through the spherical cavity and liquid can then pass from one to the other. This valve was found to hold a high vacuum against atmospheric pressure for about 1 hr. and the system pressure rose only a few millimetres Hg per day.

Note by R. H. Biddulph & P. H. Plesch *Chem. & Industr.* 30.6.1956 569

16/I

Apparatus for the Anaerobic Filling of Phials

See Abstract No.: 162/I

17/I

A Gas Introductor for a Vacuum System

Australia. A form of introductor is described where the gas comes into contact with glass and mercury only. It is claimed to be more compact than the micro-introductor of Mignolet (*J. Sci. Instrum.*, **30**, 15, 1953) but not of the same accuracy. The design incorporates a cut-off which prevents stray bubbles of gas left from a previous measurement entering the system subsequently. There is the added advantage that, when the vacuum system is raised to atmospheric pressure, the gas supply is isolated.

Note by H. A. Wyllie *J. Sci. Instrum.* 33, Sept. 1956 360-361

18/I

High-Speed Rotating Cylinder for Rarefied Gas Dynamics Research

United States. Slip flow boundary conditions have been investigated by a number of research workers in the past. Most of these consider only low surface speeds and normal atmospheric pressure. High altitude supersonic flight problems have called for reflection and accommodation coefficients applicable to these new conditions and a rotating cylinder apparatus has been designed and constructed to provide empirical data in the region of free molecular flow at high velocities. The present design was developed to enable measurements over a wide range in which the ratio of Mach. No. to Reynolds No. would be varied from <0.01 to >10. The radial gap was chosen to be $\frac{1}{2}$ inch. and this governed all other critical dimensions. The rotating cylinder has a radius of $4\frac{1}{4}$ inch. and can be rotated at controlled speeds from 4,000 r.p.m. to 40,000 r.p.m. The need to cover all flow conditions then requires operation at controlled pressures from 3 mm. Hg down to $10.^{-4}$ mm. Hg, and with a cylinder 6 inch. long the drag to be measured lies between 200 mg. and 3,000 mg. End effects are minimised by mounting cylindrical extensions above and below the floating measuring element which surrounds the mid-section of the rotating cylinder. The rotor is mounted on the axis of a cylindrical vacuum chamber 28 inch. in diameter and 24 inch. high, the motor drive being *via* an oil-sealed shaft passing through the centre of the top plate of the bell. The rotor was 60 lb. in weight, 10 inch. long and $8\frac{1}{2}$ inch. diameter. A forged aluminium alloy (17S–T6) was selected for this purpose after thorough inspection. The critical speed of the assembly was 1,000 r.p.m., a speed which is quickly passed in starting and stopping. The drag was measured by a specially designed torque balance, the drag cylinder being a ribbed, thin walled, magnesium structure, partially supported by three floats in vessels containing diffusion pump oil. The drag measuring system incorporates a Shaevitz transducer in each section and the minimum difference measurable is 1 mg. corresponding to a drag cylinder movement of 0.0005 inch. It has been found necessary to thoroughly outgas the float chamber oil before use. The system was made remote-reading and inside the vacuum bell was a $2\frac{1}{2}$-inch. thick safety shield. The whole assembly was mounted in a concrete pit for safety reasons. Rotatational speeds at Mach Nos. from $M=0.14$ to $M=0.55$ were used at pressures ranging from 0.001 mm. Hg to 0.22 mm. Hg. The oil vapour present caused the cylinder surfaces to become oily and thus limited the surface conditions which could be investigated.

Article by G. J. Maslach & J. Frisch *Rev. Sci. Instrum.* 26, Aug. 1955 751-754

19/I

Flow of Gases Through Packed Bed in Silica Powder at Low Pressures

See Abstract No.: 18/IV

I — General Science and Engineering — I

Contd.

Abstract No. and References

Leak Detection by Vacuum Techniques

20/I

United Kingdom. This is a survey of current practice in leak detection. The characteristics of the various types of vacuum gauge are first summarised, and the different methods available for leak detection are then briefly considered. The pressure rise method is one of the most obvious; the masking effect of degassing is discussed and the use of vapour traps and evacuated hoods referred to. In the second method described, the component to be tested is surrounded by a hood and both are evacuated, air is then admitted to one or the other, when a pressure change detected at the opposite side of the component will indicate a leak. Finally, the use of test gases, which enable the actual position of a leak to be located, is discussed. The gas should differ from that already in the evacuated system and should make possible the use of a selective detector. Gases are preferred to volatile liquids. The types of detectors used include the ordinary gas discharge tube, of limited pressure range and sensitivity, relying on change in colour of the glow; the Pirani type of vacuum gauge, and the various ionisation gauges. The Pirani is used in a Wheatstone bridge circuit which is balanced at the mean pressure of the system so that a sensitive galvanometer can be used to indicate transient pressure changes if the test gas (hydrogen is recommended) enters a leak. Fluctuations in the prevailing mean pressure cause difficulties and some improvement is obtained from the use of a chilled charcoal trap. Ionisation gauges, connected in the high vacuum part of a system, can also be used, although it is less convenient to get a zero reading at the mean pressure. Improved performance can be obtained from either type of gauge if a pair of similar gauge heads is used differentially, the test gas being excluded from one by a specific absorbent. The hot-cathode ionisation gauge is made more sensitive and can be used at higher pressures, if the electrode system is sealed into an inner enclosure, isolated from the main part by a palladium 'window'. This is pervious to hydrogen when heated, so that the gauge is made specifically sensitive to this gas. The difficulties attending the use of the gauge are discussed. Finally, the use of a mass spectrometer as a detector for the test gas (usually hydrogen or helium in this case) is described. The use of gaseous halides as test gases, with a diode having a platinum anode as detector, is also mentioned. The design of pumping systems for leak detection is discussed, both the straightforward system needed when the test object is to be surrounded by an evacuated hood, and the type of system for use with a test gas, which preferably has two diffusion pumps with the detector and a throttling valve connected between the two. Adjustment of the throttle so that the pressure between the two pumps is fairly high, gives a magnification of transient pressure changes occurring when a leak is probed. Some applications of vacuum leak detection are mentioned and the unit of leakage rate—the lusec—is explained.

Article by S. H. Cross & W. Steckelmacher *Research* April 1956 124-131

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Modern Methods of Leak Detection

21/I

Russia. The author reviews methods of leak detection starting with a discussion of mass spectrometer leak detectors. Basic principles of mass spectrometers design are considered classifying two types namely those with hot cathode sources and those with cold cathode sources. The latter type have a longer life but their sensitivity is lower. Whether of the 180° or sectorial magnetic analyser type the tuning is done by varying the accelerating voltage or the magnetic field. The great majority are designed for use with helium. The testing methods mentioned are (*a*) external spraying with helium (*b*) hooding with helium (*c*) filling with helium and probing externally and (*d*) leaving evacuated components in a helium atmosphere and then placing in an evacuable chamber connected to the leak detector. The sensitivity of the mass spectrometer method depends on a number of factors but is ultimately limited by the helium content of the atmosphere. The limit of detection is that the meter reading should be at least twice that due to the helium background. Halogen leak detectors are considered, especially the 'sniffer' type which is used widely in refrigerator manufacture. The same principle is used in a vacuum method in which the air pressure in the chamber is maintained at 0.1 mm. Hg and the outside sprayed with Freon. A particular property of Freon is that it has a strong affinity for oil and, therefore, can be used in the detection of leaks in oil-contaminated systems. Brief mention is made of the use of the Tesla coil in leak detection on glass systems and in combined glass and metal systems in which changes in colour of the discharge can be observed on wetting the outside surface with acetone. Pressure-testing of vessels using the soap bubble technique is also described. The Pirani gauge used as a leak detector with hydrogen as a probe gas is discussed. Ionisation and Penning-type gauges can also be used in leak detection, In particular, the ionisation gauge with hydrogen as the test gas using a special compensation circuit is described, enabling high sensitivity apparatus to be used over a wide range of pressures. The speed of reaction and magnitude of response depends on the time constant of the leak, pumping speed for test gas and ratio of sensitivity of the gauge for the test gas to that for air. The palladium-barrier ionisation gauge is described and it is observed that the sensitivity of this method in tests on hermetic sealings is considerably higher than that using an ordinary ionisation gauge connected directly to the vacuum system. The use of a magnetic-type ionisation gauge in a differential manner using butane or carbon dioxide is also mentioned. Other phenomena suggested in recent years for leak detection are listed as (*a*) change of spectrum of glow discharge in Penning type gauge with nature of gas, (*b*) coating test volume with fluorescent compound and detection of penetration by means of u.v. illumination, (*c*) observation of the u.v. absorption spectra using benzol as test liquid which produces a strong absorption at 1,790 Å. The use of radio active substances, *i.e.* carbon monoxide containing C^{14} giving β-radiation or methyl bromide containing Br^{82} giving α-radiation for leak detection in inaccessible systems is specially mentioned. Figures available on the rates of diffusion of radioactive gases in soils render the latter method of particular importance in leak detection on underground pipes.

Article by L. E. Levina *Uspekhi Fizicheskikh Nauk* 55, 1955, (1) 101-110

Testing Nuclear-Plant Leak-Tightness

22/I

United States. In designing piping for nuclear plants particular attention should be paid to the selection of components that will minimise leaks. The degree of tightness required for a nuclear system can be appreciated from a graph giving the maximum allowable primary-coolant system leakage in μc/hr. against the maximum

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permissible level in $\mu c/cm^3$. These maximum permissible levels are given in a table, reproduced below. From

*Maximum Permissible Leaks in Air**

Radioscope	*MPL* ($\mu c/cm^3$)
H^3	2×10^{-5}
Na^{24}	2×10^{-6}
K^{42}	2×10^{-6}
Cr^{51}	8×10^{-6}
Mn^{56}	4×10^{-6}
Xe^{135}	2×10^{-6}
Po^{210}	7×10^{-11}
U (natural)	1.7×10^{-11}
Pu^{239}	2×10^{-12}
Beta-gamma emitter (isotope unknown)	1×10^{-9}
Alpha emitter (isotope unknown)	5×10^{-12}

*Reproduced from Radiological Handbook, U.S. Dept. Health, Education and Welfare (1954).

such data can be deduced, for example, that a maximum leak rate for fission gases with a maximum permissible level of 2×10^{-6} $\mu c/cm^3$ (based on Xe^{135}) would be 2×10^{4} $\mu c/hr$. in a 10^7-ft^3 building. An allowable leak rate of 10^{-6} cm^3/sec. is conceivable. Hence, specialised techniques are necessary for rapid detection. Excessive leakage can produce a direct radiation hazard. A graph is given showing the dose rate that might be expected from leaks in a sodium-cooled plant. The leak-testing method chosen depends on the type of heat-transfer fluid and material of construction used. For pressurised-water and liquid-metal systems, summarised data is given comparing the mass spectromer, the halogen sniffer, the soluble-dye test, and the use of radioisotopes. The mass spectrometer is the most sensitive technique. The unit specially designed for leak-testing indicates 1 part of helium in 2×10^5 parts of air and is thus capable of detecting a leak of about 2×10^{-4} mcfh. To attain ultimate sensitivity, however, the surfaces to be tested must be scrupulously cleaned and extreme care is required. Thus, in practical field work, 0.005 mcfh is the limit. A progressive procedure making use of several tests is preferred. First a hydrostatic test with water should be used for components and sub-assemblies, then the soap-bubble test for tracing of large leaks in the assembled system. After repairing leaks so found, a hydrostatic water test should be performed on high pressure systems; exposure of the system to 1.5 times the design pressure may open up additional leaks. Finally the halogen or helium sniffer or standard mass spectromer leak testing should be applied. Details given of a case study of leak-testing an all-metal, leak-welded sodium-cooled plant of several hundred cubic feet.

Article by J. P. Verkamp & S. L. Williams *Nucleonics* 14, June 1956 54-57

23/I

A New Method for the Detection of Very Small Leaks in Pipe Systems

France. A method is described for leak detection in complicated piping systems. As they occur, in particular, in refrigerating plant, operated by condensation of ammonium gas without any moving part. Such plant consists in part of oxy-acetylene welded iron pipes in spiral shape which must be kept free of the most minute leaks and porosities in order to maintain efficiency over the years. The previous method of testing involved immersion in water and filling the system with air at 40 kg/cm^2. Small leaks giving only one bubble every few minutes are easily missed in this method. The new method provides for the filling of the system with a compressed air-ammonium gas mixture at 40 kg/cm^2 and applying a paste containing phenolphthalein to the outside of the pipes. Any leaks present cause the penetration of ammonia to the outside and this is immediately detected by a red stain appearing in the paste due to the ammonia reaction with the phenolphtalein. The actual paste used is a mixture of barium sulphate and water, to which glycerine (about 1:2) and commercial phenolphthalein solution (25 c.c. of 5% alcoholic solution for each kilogram of paste) is added. The application of the paste is as easy as that of paint.

Article by P. Niviere *Gen. Chim.* 75, May 1956 122-123

24/I

Improvements r.t. Leak Detecting Apparatus for Use with Exhausting Machinery

See Abstract No.: 74/I

25/I

Leak-Testing of Type-347 Stainless Steel Welds

See Abstract No.: 93/I

26/I

Conditioning Plant for Steam Turbine Lubricating Oils

See Abstract No.: 167/III

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Abstract No. and References

Recent Developments in Vacuum Metal Coating

27/I

United Kingdom. The author refers briefly to the relative advantages of vacuum coating and electroplating, the former being advantageous for optical finishes and where non-metallic surfaces are to be coated. The necessary high vacuum technique is then described very briefly and a schematic diagram is shown of a suitable vacuum plant. The actual coating process is likened to metal spraying on an atomic scale. The processes of evaporation and adhesion are then considered. It is usual to attempt to expose a free surface on the work by chemical cleaning followed by ion bombardment, so that the initial layers of a deposit are held in place by surface forces, or are *adsorbed*. In some cases surface adhesion is increased by the effect of electro-static double layers. As a layer builds up, the surface forces become less important and the main factor is cohesion within the deposited material itself. This tends to cause the growth of aggregates in a thick film, with an increase of diffuse as against specular reflection. It is suggested that on a crystalline surface, atoms of evaporated metal which arrive close to an atom of the crystal will be less stable than those arriving in a 'potential ditch' midway between one set of atoms. Due to thermal agitation, those atoms of the film in the less stable positions may migrate towards the others, preventing the formation of a really continuous film. Electron micrographs are shown of aluminium films condensed at different temperatures and to different thicknesses, to illustrate this point. There is a brief discussion of the stresses resulting from this tendency to rearrangement during growth of the film. The stresses have been found to increase with the m.p. of the deposited metal and to be less if the substrate is heated during deposition. Metals of low m.p. are found to form crystallites of average size about 400 Å, with a strong tendency to orientation parallel to the substrate, while those of higher m.p. are smaller (about 100–150 Å) and only weakly orientated. The author suggests that the films may be intrinsically unstable and refers to unpublished experiments he has carried out in which Al with about 30% nickel was evaporated on to a glass plate placed with one edge very close to the source. It was found that after a few hours the resulting film started to rearrange itself, forming into small rhombic plates (about 2 mm.), with clear glass between, this structure gradually spreading over the whole plate. Another example of instability given is of an aluminium film deposited in the presence of mercury vapour, which at first apparently normal and brightly reflecting, gradually changed into a grey film of aluminium amalgam. It is also a characteristic of film growth that films below a critical thickness are not (good) electrical conductors. Finally, reference is made to problems of adhesion on plastics and lacquers, where surface forces are usually small. It is suggested that this adhesion is due mainly to penetration of the metal into the soft (or softened) surface; the heat absorbed from the source as well as softening the surface, may cause evaporation of solvent or plasticiser. Thorough drying and degassing is necessary to prevent this spoiling the film.

Article by F. C. Weil *Electroplating and Metal Finishing* 9, January 1956 6-10, 25

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The Preparation and Uses of Vacuum Deposited Films

28/I

United Kingdom. The author reviews the methods of producing thin films by condensation from the vapour phase in vacuum, together with some of the applications of such films. He describes the basic processes of thermal evaporation and cathodic sputtering, and gives details of typical operating conditions. The optical properties of thin film, both opaque and transparent are discussed. The conditions necessary for the anti-reflection coating or 'blooming' of a glass surface with MgF_2 are given. For complete elimination of reflection of monochromatic light of wavelength λ_o two relations must be satisfied. Firstly the film thickness should be $\lambda_o/4$ and secondly $\mu_F=\sqrt{\mu_G}$ where μ_F and μ_G are the refractive indices of the film and the glass substrate respectively. For visual instruments using white light λ_o is chosen to be at the middle of the visible spectrum. Transparent films of ZnS which increase the reflection may also be evaporated, to give reflections of 30% in a single layer. When films of high and low refractive index are used in multilayers, the separation of reflected and transmitted colours may be enhanced. These multilayers are known as 'dichroic' filters or mirrors; they require accurate control of film thickness and are difficult to produce on large surface areas due to non-uniformity. Applications include colour television. Opaque reflecting films are usually metallic and are principally used for higher-reflecting mirror surfaces on a variety of bases. Aluminium front-surface mirrors are a typical example, as used in astronomical telescopes. The aluminium film may be protected by a transparent layer of Si0, $Si0_2$, or MgF_2 to keep the film untarnished for long periods. Uniform coatings may be readily obtained. Other applications of vacuum deposited films include metallised paper for capacitor manufacture, motor car headlamps, cheap jewellery, and aluminised C.R.T. screens. The method is in the process of developing from a laboratory technique to a commercial process.

Article by E. R. Elliott *J. Soc. Glass Technol.* 39, Dec. 1955 95N-100N

Method for the Production of Thin Layers

29/I

Germany. Both the vacuum evaporation and cathodic sputtering method have certain limitations: (*i*) Many high melting-point elements cannot be evaporated because there is no suitable material available as construction material for the evaporation source. (*ii*) Some metals treated by cathodic sputtering will not yield a deposit at all under practical conditions. These limitations are overcome by the method of the invention providing for the use of a spark generating apparatus, fitted with electrodes of the material to be evaporated. From applications of this method to spectral analysis in the past it is known that the spark causes electrode material to evaporate giving vapours consisting of multiple-charged ions and atoms formed by re-combination. By maintaining a high vacuum foreign atoms are excluded and a mirror-like adherent homogeneous layer is obtained.

L. Hiesinger & Physikalisches Untersuchungs Lab. G.m.b.H. *German Pat.* 915,765

Evaporation Source of Vacuum Evaporation by Electric Arc

30/I

See Abstract No.: 9/III

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31/I

Method of Evaporating Metals by an Intermittent Arc in Vacuum

France. It is difficult to evaporate significant quantities of typical refractory metals in a vacuum by existing methods. Electronic bombardment gives high temperatures but requires the use of high voltages. The uses of the low-tension arc in this connection, does not seem to have been widely studied. The authors give a number of experimental results which indicate that such an arc can successfully produce metallic deposits under vacuum. The initial vacuum was higher than 10^{-5} mm. Hg, the frequency of arcing was several tens of periods per second, the supply was 110V d.c., in series with a resistance of 10 Ω, the average current 10 A. The substrates were placed 7 cm. from the arc. The anode heated up more than the cathode, though it was invariably only the latter which evaporated. After a few seconds, an opaque deposit of metal was obtained. Successful evaporations were achieved with C, W, Pt, Ir, Au and Zn, whereas copper and aluminium did not evaporate well. Voltages of about 1,000V were applied to the plates, to study the nature of the evaporated particles, With the voltage positive, almost the whole of the evaporated metal was observed to concentrate on the substrate. This could be a distinct advantage in the case of rare or precious metals. The concentration observed indicates the presence of negatively charged metallic particles in the vapours—pointing at least partially at a mechanism analogous to that of cathodic sputtering.

Letter by B. Vodar, S. Minn & S. Offret *J. Phys. Radium* 16, Oct. 1955 811-812

32/I

Evaporation from an Electric Arc in Vacuum

See Abstract No.: 8/III

33/I

The Applications of Vacuum Techniques to Certain Methods of Depositing and Melting Materials

France. The author presented this paper at the International Congress for Materials and Aviation and Guided Missiles in 1955. The introduction is concerned with the kinetic theory of gases, molecular structure, gas pressure, mean free paths, etc., and a survey of pumps. This is followed by a description of plant employed by the radio industry for the coating of piezoelectric crystals. The use of Araldite B resin in glass-metal seals is mentioned with special reference to its high resistance, good insulation and heat-resistance. The application of the Dalic plating process to the joining of broken tungsten filaments is indicated briefly. Special crucible techniques developed by Philips are also mentioned.

Article by R. P. Henry *Met.-Corr. Industr.* 31, June 1956 274-288

34/I

Vacuum Metallisers Reach New Markets

United States. Vacuum-deposited films, once considered mainly as a decorative finish, are being used increasingly for applications requiring coatings of specific properties. In addition to low cost per part and light film weight, vacuum-deposited films have good adhesion to a wide range of materials including metal, wood and plastic. They conform closely even to sharply changing contours and leave no corrosion residues. Almost every known metal and some alloys can be evaporated to form coatings. Non-metals are usually deposited as metallic salts. A thin, uniform film controllable within very close limits is obtained. In the optical industry films of magnesium fluoride are vacuum-deposited on camera and binocular lenses to prevent glare, and metal coatings are used on interference filters and graded density sunglasses. 'Metallised' films of closely controlled thickness are used in precision resistors, and miniature electrical components make use of very thin, conductive films. Transparent, hard coatings of titanium oxide or silicon monoxide can be employed to protect softer materials. 'Metallised' films used in conjunction with appropriate organic top coats have, in some cases, given better results than copper-chromium electroplated finishes in certain laboratory abrasion tests. The corrosion resistance of the films is high and they can be used to protect metal parts where the possibility of hydrogen embrittlement rules out other coating methods. When the surfaces are sufficiently clean a molecular bond is obtained between the 'metallised' coating and the substrate. As a result of coating it may be possible to solder substrate materials which are otherwise difficult to join. The freedom of vacuum-deposited films from gas is an advantage in parts to be used for electron tubes. Metallising can give a mirror-bright finish and under carefully controlled conditions aluminium films with a reflectance of 98% have been obtained. Decorative aluminium finishes can be produced which closely simulate the appearance of other metals such as gold, copper or silver. This effect is obtained by applying a clear or tinted lacquer or enamel top coat to the metallised film. Decorative pieces can be made by coating the inner surface of acrylic or polystyrene plastic which has been moulded or embossed to the required pattern. A typical metallising plant consists of a 5½ ft. dia. steel tank with a high-temperature evaporation source situated along the central axis. The parts to be coated are supported on a series of rods arranged radially. Each rod revolves around the evaporating source, spinning on its own axis at the same time. The pumping system may comprise several diffusion pumps plus a large mechanical roughing pump. Evacuation times of 4-8 mins, with total cycle times of 7-10 mins. are possible. Equipment is also available for continuously coating rolls of plastic, paper or textiles. The resulting materials are used in heat-reflective safety clothing, electrically conductive films for radar reflection, electrostatic shielding and for decoration.

Article by P. J. Clough & J. H. Durant *Iron Age* 6.9.56 91-94

35/I

Finishing of Metal Objects by Metallisation in Vacuo

France. Vacuum-metallised metallic articles, particularly zinc die-castings of motor car parts (e.g. door handles, exhaust pipes, headlamps, radiator grills, etc.) show improved resistance to atmospheric humidity and greater electrical conductivity, in some cases withstanding salt spray tests of 800 hours duration without deterioration. Prior to the coating treatment the articles are phosphatised and lacquered to provide a smooth surface and

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reduce the pumping time required. After firing at 149°C for 20 min. the articles are placed on racks and introduced into the vacuum chamber which is then exhausted to 0.5 μHg. Degassing of the aluminium metal prior to evaporation by pre-heating is advocated. Final lacquering is advisable and a protective layer of 50-75 μ thickness is satisfactory.

Article by Anon. *Galvano* January 1956 35-38

Coatings for Vacuum Metallised Plastics 36/I

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Laminated Thread 37/I

See Abstract No.: 20/III

Improvements i.o.r.t. Processes for the Production of Thin Flexible Glass Coatings on Wires, Foils and Similar Supports 38/I

Germany. Wires, foils etc. coated with an ordinary insulating material cannot normally be operated at temperatures exceeding 80–100°C. This temperature could be exceeded if an impervious, homogeneous coating of glass was applied, and flexibility could be maintained if the coating was thin, preferably of the order of 10 μ. Previous methods of coating with glass have been unsatisfactory for the following reasons: (*i*) vacuum evaporation is impracticable as 'fractional distillation' of the glass occurs unless special steps are taken to prevent it; (*ii*) electrophoresis does not produce a completely impervious thin coating. A new method is proposed whereby at least one, or alternatively all components required to form a glass coating are separately applied to the article by evaporation in vacuum. For example, a material such as silicon, boron or phosphorous which forms glass acid is first evaporated on to the support. This material is converted into a thin glass coating by oxidation, usually by heating in an oxygen-containing atmosphere. This glass coating may consist of vitrous silicic acid and/or vitreous boric acid. Or, after the vacuum evaporation, the coating is converted into a vitrous metal silicate or metal borate by heat treatment (a copper silicate or borate coating being formed if the support contains copper). The process produces a coating which is reasonably flexible without the glass cracking or flaking off and is relatively simple to perform. The process is particularly suitable for producing a good insulating coating on electrical wiring or on foils used in electrical condensers.

Siemens-Schuckertwerke *Brit. Pat.* 738,357

Trends in Metallurgical Research in the United States 39/I

United States. The chief lines of metallurgical research in the U.S. are reviewed. A new apparatus for measuring elastic strain and stress patterns is the Norton Geiger-counter diffractometer. Electronic methods of recording x-ray intensities now make it possible to determine steep composition gradients as in diffusion. A radioactive isotope method is in use at the Massachusetts Institute of Technology for the rapid determination of self-diffusion. The development of curved crystal analysers has improved the x-ray fluorescence method of analysing steel, and a 3-channel curved-crystal spectrometer can be used for the simultaneous determination of chromium, nickel and molybdenum in steel. X-ray analysis of steel using vacuum or helium filled optical paths is a possible future development to permit the analysis of low-atomic number elements. Studies on metal structure have revealed a martensite like transformation in sodium at −400°F. The first small transformation is revealed by the geometrical roughening of a highly specular surface which is obtained by melting sodium in a short glass tube into which it was vacuum distilled and sealed. Two theories are held as to the nature of martensite: one explains the transformation as a simple nucleation and growth mechanism: the other considers the martensite nuclei as strain centres which contain sufficient energy to initiate a co-operative displacement among the austenite atoms. Research is also being carried out on the mechanism of tempering and on the boron effect. A new method of preparing metal specimens for the electron microscope has been developed by R. M. Fisher. A conventional plastic replica is applied and then the surface is re-etched through the replica which is permeable to etching solutions. Particles of the segregate phase are undermined and adhere to the replica upon stripping. The method thus provides a conventional replica of the topography of the surface and also actual particles suitably mounted for study by the electron microscope or by electron diffraction methods. Observations on growth spirals have included a study of the spiral formations obtained during the growth of cadmium crystals from vapour at controlled supersaturation in a special growth cell. Filamentary crystals of 'whiskers' have been grown under special conditions and their usual strength, which approaches the theoretical value for the perfect crystal, indicates that they are nearly free of dislocations and might serve as seeds on which to grow exceedingly strong macroscopic filaments. By using zone melting to purify germanium impurities such as phosphorus, antimony and arsenic have been reduced to an estimated value of 1 atom in 10^{10}. At the Carnegie Institute of Technology the Knudsen cell is being used to measure the vapour pressures of alloy components and carbides. From these the thermodynamic activities can be calculated. The cell consists of a cylinder with a small knife-edged orifice in the top. The material to be studied is placed in the cell and heated in a vacuum to induce volatilisation. The pressure can be calculated by the Knudsen equation from the amount of material escaping through the orifice in unit time. A radioactive tracer method of measuring this escape permits the measurement of pressures as low as 10^{-9} atmospheres. The determination of hydrogen in a steel sample by solution in liquid tin and analysis of the evolved gas has been improved by collecting the gas at a pressure of 1–2 mm. Hg and introducing it into a hot-wire gauge. The current required to heat the wire to a given temperature depends upon the thermal conductivity of the gas which in turn is highly sensitive to its hydrogen content. A direct measure of the hydrogen content can be obtained in this way.

Lecture by E. C. Bain *J. Iron Steel Inst.* Nov. 1955 193-212

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40/I	**The Present State of the Industrial Vacuum Melting Processes** See Abstract No.: 87/III
41/I	**Why is the Big Money Behind Vacuum Metals** *United States.* Some of the American firms which carry out vacuum melting or provide equipment for vacuum melting are named. An outline is also given of the German Bochumer process for the vacuum degassing of steel. Among the leading suppliers of vacuum melting equipment is the Consolidated Vacuum Corp., which has built production units for Carboloy and Westinghouse. The National Research Corp. has produced a vacuum unit of 2,200 lb. capacity for the Vacuum Metals Corp., and has acquired the U.S. licensing rights to the Bochumer process. The F. J. Stokes Machine Co. has built pioneering installations at the Utica Drop Forge and the Universal Cyclops companies. Allegheny Ludlum is making cast electrodes of a predetermined alloy composition from a production size, electric furnace air melt. These electrodes are then remelted under vacuum by arc melting in a water-cooled copper crucible. The success or failure of vacuum techniques is not, primarily, a question of metallurgy but of the effectiveness of the equipment. Vacuum melting does not dispense with the need for good melting practice. An important factor in vacuum melting is the vapour pressure of the various metallic elements. If the vapour pressure of a metallic element is low, oxides of the metal decompose at the melting point of the metal and the released oxygen is pumped away. Because of this, nickel alloys can be made under vacuum with practically no slag. If the vapour pressure of the element is extremely high, as in the case of manganese, it is difficult to keep the element in the melt. In vacuum degassing the entrapped gases are removed after melting down. Three methods have been developed by Bochumer Verein. In one, the least effective, the pouring ladle containing liquid steel and a slag cover is placed in a vacuum chamber. In the second, an empty ladle is placed in a vacuum chamber and a special tapping ladle is tightly sealed into the chamber. Fluid steel pours from the tapping ladle into the evacuated chamber in a controllable stream of individual droplets. In the third method, the droplet stream is fed directly into an ingot mould in the vacuum chamber. The second and third method can be used to handle heats up to 150 tons. Mould coatings and trouble due to metal splash on the ingot mould walls are eliminated. The vacuum ingot process has greatly reduced, or eliminated, flaking on the German Ni-Cr-Mo steels which have been tested. Results have still to be obtained, however, on U.S. grades of steel. A similar improvement in the mechanical properties of steel is obtained by either vacuum melting or vacuum degassing, except in the case of impact strength which is greater for vacuum-melted metal. Vacuum melting is expected to be used for specialised materials, such as aircraft materials, and vacuum degassing for high-tonnage requirements—for example the production of massive ingots for extremely large forgings. Article by P. M. Unterweiser *Iron Age* 26.1.1956 67-72
42/I	**Economics of Investment Cast Vacuum Alloys** See Abstract No.: 183/I
43/I	**Why Melt Metals in a Vacuum?** *United States.* Vacuum melting is employed generally to combat the effect of gases in the metal. Alternatively, the gaseous atmosphere, or the slag, may react with elements of the alloy to produce undesirable properties; this, too, may be avoided by melting *in vacuo*. An important example is the production of alloys for jet-engine turbine blades; these must have high strength at elevated temperatures and 2–5% of titanium is used as an alloying element to produce this property. The amount of titanium that could be used was limited while the alloy was melted in air because of the formation of titanium carbonitrides; these tended to weaken the alloy in subsequent fabrication. Vacuum melting eliminates this difficulty and permits the production of alloys with a greater titanium content. Moreover, the alloys produced have more uniform properties. Vacuum melting is used in the production of titanium and facilitates the removal of hydrogen, the presence of which had previously been responsible for the delayed fracture of components made from titanium alloys. This technique has also been used for the production of steel for ball-bearings. More uniform properties have resulted in an increase in the average life of the bearings to a value equal to the maximum life of bearings made from steel melted in air. Melting *in vacuo* facilitates the removal of hydrogen and nitrogen from the metal. In order to remove oxygen it is necessary for carbon in the metal to react with the oxygen to produce carbon monoxide, which is then pumped away. Volatile metals and salts also may be removed during the process. Induction and arc melting are compared. The advantages of the former are that the metal can be kept molten for as long as desired, the charge can be of any size, several ingots of different sizes and shapes can be poured from a single heat and various reactions can be programmed during the melting. The technique of arc melting *in vacuo* differs from that used in air. A consumable-electrode is used and the crucible is water-cooled copper. There is thus no reaction with a ceramic crucible as there is with arc melting in air or with induction heating. Thus titanium, zirconium and molybdenum, which react rapidly with ceramics, are arc melted. Arc melting is faster than induction melting but the need to have the charge in the form of a consumable-electrode is often a limitation. There appears to be little to choose between the two methods as regards the quality of the product. The article discusses vacuum melting equipment and particularly the pumps required; these must handle large quantities of gas. Larger pumps, or pumps more efficient at about 1 mm. Hg are required for arc melting because of the rapid melting rate. Pumps efficient at lower pressures (1 to 100 micron Hg) are more often needed for induction melting. Attention is drawn to the fact that there are serious difficulties in using vacuum melting for some metals and alloys. Article by G. W. P. Rengstorff *Battelle Tech. Rev.* 5, May 1956 3-6

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Vacuum Melting Furnaces—An Interim Report

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The Bochumer Verein Vacuum Casting Process

45/I

Germany. Work on the vacuum casting of steels was started in 1950 and now casting can be carried out on an industrial scale. The gas content of steel greatly affects its quality. Hydrogen is the most troublesome gas but oxygen and nitrogen also have an effect. The hydrogen enters the melt through moisture in the air, through additions of ores, through rust, moisture and oil on scrap, through the producer gas used for heating and finally during the casting, as the metal passes from the spout and ladle into the target mould. The solubility of hydrogen in steels falls from 0.3 cm.^{3}/gram. at 1,600°C to 0.0089 cm.^{3}/gram at 1,200°C. As the steel cools, therefore, hydrogen comes out of solution. Bubbles of gas can pass through the solidifying melt leaving the much feared shadow lines along which the physical properties of the steel are often inadequate. Also molecular hydrogen can accumulate under very high pressure at places within the ingot and cause an internal rupture in a previously sound structure. These cracks may be removed by prolonged heating and forging operations, but in vacuum casting they are largely avoided. The tendency of alloying elements such as vanadium, titanium, niobium and aluminium to oxidise is also eliminated in this casting method. Owing to the difficulty of putting a large furnace under vacuum, degassing is carried out after melting in one of three vessels. Two of these are 2.4 metres in diameter and 4.2 metres high and the third is 4.4 metres in diameter and 9 metres high. They are attached to a central pumping station fitted with high vacuum pumps. Preliminary experiments were conducted with 10 kg. ingots and water jet pumps, but the water from the pumps caused trouble in the determination of the hydrogen content of the metal. Three methods of degassing are used depending on the requirements. (*i*) Ladle degassing (*ii*) Degassing during pouring. (*iii*) The casting *in vacuo* of ingots up to 150 tons. In the first method, a ladle of the material is rapidly evacuated. The emergence of the gas from the molten metal can be observed through a quartz glass window equipped with a device for cleaning off any deposit formed during the process. Higher degassing values are achieved by pouring the metal from one ladle to another under vacuum. The stream of metal is torn apart by the evaporating hydrogen and falls in droplets into the second ladle. High speed cinematography has been used to study the phenomenon. In the second method, the aluminium gaskets sealing the vacuum chamber are melted by the heat of the liquid metal. Special ladles have been developed so that the steel does not have to be made too hot before treatment. A 40 ton charge cools by 30°C during a pouring treatment lasting 8 minutes. The metal is subsequently cast in air. The conditions of work for a team casting metal under vacuum (the third method) are much better than when casting in air and also the actual process can be more easily observed and controlled. Temperature measurements are made with specially sheathed platinum-platinum/rhodium thermocouples fixed in the ladle. The temperature indications of this pyrometer are continuously recorded. Analysis of the atmosphere in the degassing chamber shows virtually complete absence of oxygen. Mean values of analysis show:—Hydrogen 20%, CO 45%, CO_2 5% with nitrogen making up the balance. Much work on finding the optimum conditions for vacuum casting has been carried out, yielding clear improvements in product quality. At the time of writing Bochumer Verein is the only plant at which vacuum casting can be carried out on this large scale, but world interest in the technique is increasing.

Article by A. Tix *Hüttenzeitung* 3, 1954 Translated by B.I.S.R.A. & *Stahl u. Eisen* 76, January 1956 & *Iron & Stee* March 1956 81-85

Metals of High Purity

46/1

United Kingdom. Extremely pure metals are essential to the electronics industry which manufactures semiconductor devices like the transistor. Knowledge about the behaviour of such metals is basic to metallurgy and their mass production on a tonnage basis may become important to industry. Methods of purification can be classified as chemical or thermal. The chemical processes depend on the production of a pure compound of the metal and its subsequent reduction. Production of the pure compound can be by the following methods:—(*1*) Repeated precipitation; (*2*) Repeated recrystallisation; (*3*) Precipitation of impurities as insoluble compounds; (*4*) Fractional distillation; (*5*) Solvent extraction; (*6*) Ion exchange processes. Contamination of the material can be due to the reagents used, from the reaction vessels, and from the trays in which the pure compound is reduced to the metal. Extreme care in reagent purification and the 'conditioning' of container enables very pure metals to be produced chemically. Table 1 summarises the potentialities of chemical purifi-

Metals Reduced From Compounds Purified by Various Methods.
Metallic Impurities in Parts per Million.

Repeated Precipitation	*Repeated Crystallisation or Ion Exchange*	*Precipitation of Impurities*	*Fractional Distillation*	*Solvent Extraction*
Ag 10	La 20 Ce 20 Nd 30 Y 30	Co 10 100* Fe 10 100* Ni 10 100* Pt 10 10* Pd 10 10*	Ge 0.1 Si 0.5	Ga 50

*Gases (O+H+N) in ppm.

cation. There are six basic thermal purification methods. (*1*) Fire-refining oxidation of impurities which are fluxed away. This method is limited in its scope but will produce very pure gold and silver and is widely used

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in the preparation of commercial lead. (*2*) Large scale fractional distillation produces high purity zinc, magnesium, cadmium and mercury. (*3*) Vacuum distillation is the process used to produce pure alkali metals. (*4*) The Van-Arkel iodide process operates by the selective distillation of a pure iodide of the metal. (*5*) Electrolysis produces pure copper, iron and aluminium. Re-refining is common, using progressively purer electrolytes at each stage. (*6*) Zone melting provides the pure germanium and silicon needed for semi-conductor devices. A recent development of the technique avoids possible contamination of the metal from the container by arranging the heating so that a shell of solid metal remains around the molten zone. (*7*) Vacuum melting removes oxygen, nitrogen and hydrogen from the metal. Melting is achieved using consumable electrodes and a water cooled copper hearth which produces a minimum of contamination. The results that can be achieved by thermal processes are summarised in Table 2. The future may see the reduction of the general level of impurity by a factor of ten within

Metals Purified by Various Refining Methods.
Metallic Impurities in Parts per Million.

Oxidation and Fluxing		*Fractional Distillation*		*Van Arkel (Iodide) Process*			*Electrolysis*		*Zone Melting*		*Vacuum Melting*		
Ag	10	Cd	10	Cr	200	50*	Al	30	Al	—	Cu	10	10*
Au	10	Hg	5	Hf	130	50*	Cu	10	Bi	—	Fe	10	10*
Pb	30	Mg	50	Th	—	50*	Fe	10	Ga	—	Ni	10	10*
		Zn	10	Ti	—	50*	Cr	50	Ge	0.1			
		Ca	10	Zr	—	50*			In	—			
		K	10						Sb	—			
		Li	10						Si	0.1			
		Na	10						Te	—			

*Gases (O + H + N) in ppm.

Article by J. C. Chaston *Metal Progr.* 69, Jan. 1956 64-67

the next decade and the development of new methods of measuring impurity contents.

47/I

The Procurement of Some Hitherto Rare Metals

United Kingdom. Many of the so-called rare metals are now being used industrially. The annual production of titanium is about 20,000 tons, and of zirconium 150 tons, and uranium, beryllium, niobium, and possibly vanadium, have an annual output of many tons. The rarer metals cannot be obtained in a pure form direct from the ore, but have to undergo an intermediate conversion into an oxide or halide. A list is given of the sources of the rarer metals. Their preliminary treatment may be decomposition with alkalis, attack by acids, reduction with carbon and chlorination, smelting and roasting and sublimation of oxides. The methods for obtaining pure compounds include: Distillation of chlorides, sublimation of chlorides, sublimation of oxides, solvent extraction, ion exchange, fractional crystallisation, fractional precipitation, formation of amalgams, and chromatographic techniques. The metals may be obtained from these pure compounds by reduction of oxides with hydrogen electrolysis of aqueous solution, thermal dissociation of iodides, reduction of halides with another metal, reduction of oxides with another metal, and oxide-carbide reaction *in vacuo*. Reduction of halides by another metal can be used where the excess of reducing metal can be eliminated by vacuum distillation, only calcium, magnesium, sodium and lithium are obtainable in a sufficiently pure state. Absence of nitrogen is essential. Magnesium is used to reduce titanium, zirconium, and hafnium tetrachlorides, and beryllium from sodium fluoberyllate. Thorium and uranium fluorides, and all the rare earth fluorides except samarium, europium and ytterbium are reducible by calcium, but lithium is better for the rare earth fluorides, being more easily and completely eliminated in excess by vacuum distillation. The impossibility of obtaining samarium, europium, and ytterbium by reducing their halides with another metal is due to the stability of their divalent salts. The metals may be obtained by heating their oxides with excess of lanthanum *in vacuo* at 1,200°C. The sublimed metals are condensed on a cool tantalum sheet. To reduce niobium pentoxide to metal, it is mixed with the stoichiometric quantity of niobium carbide, pressed into bars, and heated in high vacuum at 1,600°C until no further carbon monoxide is evolved. The porous brittle crystalline sponge, containing unreacted carbide and oxide, is broken up, re-compressed and heated in high vacuum near the melting point. Any excess of oxide and impurities are thus volatilised.

Article by A. R. Powell *Chem. & Industr.* No. 31, 11.8.1956 809-812

48/I

Freeze Drying I. Introduction

See Abstract No.: 20/IV

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Freeze Drying II. Small Scale Freeze-Drying in the Laboratory

See Abstract No.: 21/IV

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Freeze Drying III. The Preservation of Micro-Organisms

See Abstract No.: 24/IV

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Freeze Drying IV. The Preservation of Tissues — 51/I

See Abstract No.: 34/IV

Freeze Drying V. Freeze Drying as a Large-Scale Operation — 52/I

See Abstract No.: 38/IV

Purine Compounds in Snake Venoms — 53/I

Australia. Adenosine was identified in the venom of two African snakes, *Bitis arietans* and *Dendraspis viridis*, by Fischer and Dörfel. No other nucleoside or nucleotide was present, though traces of a guanine compound were not excluded. The author has identified adenosine 3′—phosphate in addition to adenosine in the venoms of three out of eight Australian snakes, Notechis scutatus, Denisonia superba and Aconthophis antarctica. The venoms of these snakes are vacuum dried after collection and preserved over cadmium sulphate for immunisation studies. The whole venom, a fraction soluble in 50% methanol and the product of dialysis of the venom *N. scutatis* were examined by paper chromatography, using the photographic technique of Markham and Smith, and quantitative analysis of all three venoms was carried out by dialysing, freeze drying the diffused products reconstituting in 0.04 *N* hydrochloric acid and examining in a Beckman spectrophotometer. A component which might be either guanosine 2′–or 3′–phosphate was noted in the venom of *N. scutatus*. It is concluded that these compounds, as those in the African venoms, are probably natural constituents of the venom and that they arise directly from the venom glands, which may well yield neucleotides additional to those already identified in the glandular secretions.

Letter by H. M. Doery *Nature* 177, 25.2.1956 381-383

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Preservation of Animals and Plants by Drying from the Frozen State — 54/I

See Abstracts No.: 39/IV

A Cell for Kinetic Measurements of Gas Evolution from Systems Irradiated by Fast Electron Beams — 55/I

United Kingdom. By employing a mercury bellows manometer and balancing circuit it has been found possible to measure rapid rates of gas evolution from systems undergoing decomposition under fast electron bombardment from an electrostatic generator. The apparatus is reasonably robust, rapid in response, and gives reproducible results. Much slower rates of gas evolution can also be measured by the same technique.

(*Authors*)

Article by C. B. Amphlett & T. F. Williams *J. Sci. Instrum.* 33, Feb. 1956 64-65

13 — ELECTRICAL SCIENCES — 13

Arcs in Vacuum — 56/I

United Kingdom. Experiments have been conducted to determine the bahaviour of electric arcs in vacuum. The anode used in each case was a flat steel disc 2 inch. in diameter and the various cathodes were about 1 inch in diameter except for wires used in the case of nickel and gold. It was found that arcing voltages, though ragged, depended on cathode material (see Table reproduced below) and that the voltages did not change when the

Cathode material	*Arc voltage (volts)*
Cadmium	10
Magnesium	12
Gold	12.5
Nickel	15.5
Silver	16.5
Aluminium	19.5
Carbon	20
Copper	21
Steel	33
Tungsten	>50

anode became coated with vapour. Arc voltages were found to be very nearly independent of arc current. All metal cathodes showed microscopic melting, carbon was found to be pitted. By the use of evaporated metal film on glass cathodes clear cathode tracks could be obtained.

Letter by M. P. Reece *Nature* 177, 9.6.56 1089-1090

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57/I
Article by N. Calinicenco C. Ruxior & C. Ciobanu
Bull. Inst. Polit. No. 1-2, 1955 25-31

The Transport of Matter in the D.C. Arc

Roumania. The authors have studied the transport of matter in an arc between copper electrodes, employing the Petrov type of arc discharge, and alternatively a sparking arc. In the Petrov arc the transport of electricity is effected by a flux of electrons and positive ions, whereas the matter is transported from the cathode to the anode. The amount of matter eroded is a function of the number of sparks. At the same time the active oxidisation of the anode makes the disintegration of the matter easier.

(*Authors*)

58/I

Anode Temperatures and Characteristics of the D.C. Arc in Noble Gases

United States. Preliminary experiments using a disappearing filament optical pyrometer on the graphite electrodes of a d.c. arc in air, helium and argon, both with and without spectro-chemical samples in the anode crater, showed that it might be possible to relate some of the phenomena observed to the temperature of the electrodes. The present paper describes further work using arcs in noble gases alone, without any material in the anode crater. A disappearing filament pyrometer was thought unsuitable for this work, due to the long time taken to obtain a reading and the variability of readings among different operators. A continuously recording optical pyrometer was, therefore, made, using thermistors in a Wheatstone bridge circuit. Light from a point 4.5 mm. from the tip of the graphite electrode was focussed onto a slit. Light passing through this slit was focussed onto one of the thermistors, the other being kept in the dark. The thermistors (Western Electric type 23 A) were chosen because of their low thermal capacity and the pair used were also chosen to have equal resistance at the current (1 mA) at which they were operated. This pyrometer was calibrated against a disappearing filament pyrometer by taking the readings of both on a tungsten filament lamp. The total estimated error, as recorded, relative to true black body temperature with the thermistor device, was $\pm 50°C$ when all sources of instrumental and calibration error were taken into account. The arc itself was struck between graphite electrodes in a demountable vacuum tight chamber. The cylindrical walls of the chamber were of nickel-plated brass and carried four 4 inch. × 1 inch quartz windows. The electrodes were attached to either end of the chamber by water-cooled collets which also carried a passageway through which the chamber could be evacuated or the test gas introduced. The chamber pressure was measured by a mercury manometer. No difference was found in the behaviour of spectroscopically pure and ordinary spectroscopic graphite rods. Experiments were conducted in helium, air, neon, argon and krypton. A temperature *vs.* time graph shows that the equilibrium temperatures of the anode and the random variations about these temperatures are characteristic for each gas. Graphs connecting the voltage across and current in the arc, power input and electrode temperature are given for arc gaps of 4, 6 and 8 mm. An explanation of some of the phenomena observed is offered in terms of the collision cross sections of the molecules of the gases at the temperature (about 6,000°K) of the arc plasma.

Article by B. L. Vallee & M. R. Baker
J. Opt. Soc. Amer. 46, Feb. 1956 77-82

59/I

The Stability of Thermistors

Australia. In spite of the wide use of thermistors for temperature measurement, little information is available as to their stability. Greenhill and Whitehead state that, by calibration of the instrument after each experiment, errors due to variations in cold resistance may be reduced to about 2% in measuring temperature differences of 0.01°C. Doucet gives an accuracy limit of 0.002°C using bead type thermistors whilst Stanley found variations of 0.4°C over a long period when using rod-type thermistors. The author shows that, although these units may be unreliable for measuring absolute temperatures over long periods they can, within certain limits, be relied upon to give relative temperatures to an accuracy of 0.02°C. The experiments reported here, make use of glass enclosed, directly heated, bead-type thermistors the resistances of which are measured using an a.c. bridge. The relation between the resistance R and temperature T of the bead, may be expressed by $R = ae^{b/T}$ where a and b are the 'constants' of the thermistors. These 'constants' are in fact functions of the temperature and, for an accuracy of 0.01°C, each pair of values used is applicable only over a temperature range of 6–12°C. The figures quoted by the author refer to field measurements of the temperature of 2 inch. diameter, water-filled, boreholes of depths between 200 and 800 ft. Two sets of calculated temperatures are given, one set based on derivations of the thermistor 'constants' before leaving the laboratory and another set on similar values measured after returning from the field two months later. In all cases there is a marked increase in the values calculated from the second calibration as compared with the first, showing that the values of a and b changed considerably over this two-month period of use. Relative temperatures at different depths are, however, remarkably constant. A further series of checks carried out in the laboratory over a period of 17 months shows that the error in calculated temperature increases as the measured temperature increases and that if the thermistor is subjected to mechanical or thermal shock or to a maximum elevation of temperature higher than that for which it has already been calibrated, its behaviour may change abruptly. The general tendency of the thermistor used has been to show a rise in resistance and thus an increase in error with time. In general it can be stated that although thermistors may reach a state where their 'constants' remain stable, they may later undergo a change which takes place in an arbitrary manner. Adverse heat treatment may be one cause of variation and the units should not be subjected to temperatures outside the range to be used. Present results show that it would be unwise to use two or more different thermistors to measure temperature difference in one experiment without careful calibration of each thermistor both before and after the experiment.

Article by A. Beck
J. Sci. Instrum. 33, Jan. 1956 16-18

60/I

Diffused Emitter and Base Silicon Transistors

United States. For good high-frequency characteristics junction transistors require narrow base regions (of the order of a few microns thick). Diffusion from the vapour phase of a suitable impurity into a parent crystal allows a thin layer to be made in a controllable manner. This layer can then be used as the base layer of a transistor,

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the parent crystal being the collector. Double diffusion of two impurities, possibly simultaneously, allows the emitter to be a diffused region also, on top of the base layer. In the *n-p-n* silicon transistor described antimony and aluminium were used as the diffusing elements. Contact to the collector was made by alloying to a gold antimony plated metal tab. Aluminium was evaporated through a mask on to the emitter to give a line 0.005×0.015 cm. laterally and 10^5Å thick. This was then alloyed through the emitter layer to make electrical connection to the base, *via* a tungsten pressure point. A gold-antimony plated tungsten point was used as a pressure contact with the emitter. With a base layer thickness of 3.8×10^{-4} cm. an alpha cut-off frequency of 120 Mc/s was obtained, the collector capacitance being 0.5 $\mu\mu$F at $V_c = 10$V. Dissipations up to 400 mW could be obtained. A discussion of the theory of the structure is given in which it is explained that the non-uniform distribution of impurities in the base region gives rise to electric fields. These fields increase the cut-off frequency, and affect the emitter efficiency and other parameters.

Article by M. Tanenbaum & D. E. Thomas *Bell Tech. J.* 35, Jan. 1956 1-22

A High-Frequency Diffused Base Germanium Transistor

61/I

United States. The production of the narrow base width needed for high frequency transistors can be achieved by diffusing a suitable impurity from the vapour phase into a parent crystal to form a thin base layer. In the *p-n-p* germanium transistor described the parent *p*-type crystals were placed in a vacuum oven for the diffusion process. Baking out was performed at 1,900°C, and the diffusant, arsenic, was diluted with germanium. The emitter was made by evaporating a film of aluminium (1,000 Å thick) onto a small part of the diffused base layer, and the aluminium was alloyed into the base region. A similar film of gold-antimony alloy was evaporated on to the base layer near the emitter, to provide the base contact. Pressure points were used for the emitter and base, and the collector (the parent crystal) was soldered to a metal tab. Transistors fabricated by the method described had alphas of 0.98 and alpha-cut-off frequencies of about 500 Mc/s. The collector capacity was about 0.5 $\mu\mu$F at $V_c = -10$V, and the collector and base spreading resistances were each about 100Ω. It is shown that the non-uniform distribution of impurities in the base region does not have a very large effect.

Article by C. A. Lee *Bell Tech. J.* 35, Jan. 1956 23-34

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Effect of Vacuum Heating and Ion Bombardment of Germanium on Point Contact Rectification

62/I

United States. The Mott-Schottky theory predicts that the temperature dependence of the low-level resistance of a metal-to-semiconductor point contact would depend on the work function of the metal used, but experiments have failed to confirm this. The results reported in this paper show a similar null result after various vacuum treatments of the germanium. Furthermore, it has been suggested that adsorbed gas is necessary for point contact rectification to occur; the results in the paper suggest that thermal history is more important. The experiments used a slab of single-crystal Ge, top surface parallel to (111) planes, resistivity 12 ohm-cm (*n*-type). The slab is supported by graphite and quartz (to minimise contamination) from a Mo slab which can be heated by electron bombardment. Two alternative catswhiskers were used, each being formed from a V-shaped piece of 0.004 inch wire, one of tungsten and one of columbium, metals having different work functions but similar mechanical properties. Either of these could be arranged to press on to the Ge surface so that the apex of the V formed a contact less than 0.008 cm. in diameter with a contact force of 3 g, or somewhat larger with 18 g. To obtain a diode characteristic, current was passed between either catswhisker and the Mo mounting slab, the potential of the Ge being obtained by a probe resting on the surface. The whole apparatus was contained in a tube pumped by a 3-stage diffusion pump through a liquid N_2 trap, and a Mo film getter was also used. The pressure was measured by an ion gauge of the Bayard-Alpert type, pressures below 5×10^{-9} mm. Hg being claimed. Ar gas could be admitted via a metal vacuum valve. It was found that if the Ge was allowed to cool after heating to above 800°C, the ratio of forward to reverse currents at 1.0V and 20°C was less than 1.2 and that subsequent exposure to dry 0_2 at atmospheric pressure for ½ hr. had very little effect. Even heating the Ge to 500°C for ½ hr. in a residual pressure of 5×10^{-5} mm. Hg after pumping away the 0_2 (without getter) gave little effect. Vacuum annealing at 500°C and 10^{-6} mm. for 10 hr., however, caused the ratio to increase to about 28, and it was found that alternative heating to 800°C and annealing at less than 5×10^{-8} mm. gave a cyclic change in rectification ratio. Another treatment was to bombard the Ge with 0.1 mA of Ar ions at 600V. This reduced both forward and reverse currents, but the ratio increased to about 40. A short anneal (10 min. at 500°C and 1×10^{-8} mm.) then produced only a very slight change, but prolonged annealing caused a return to the state obtained by heating and annealing only. The condition produced after the ion bombardment and short anneal, which gave the best rectification is believed to approximate to that given by a pure Ge surface. No significant difference was found between the characteristics for the two different catswhiskers, nor did heating them to 2,000°K for 1 hr. at 5×10^{-8} mm. have any effect. After a total of over 200 hr. above 500°C and over 75 hr. at over 700°C, the resistivity had not changed significantly. It is concluded that the best rectification is obtained with the cleanest surface and the best lattice structure. The low-level resistance measurements were made with applied voltage below 10 mV, the temperature being varied by means of an oven, and log res. being plotted against q/kT; a 'diode activation potential' is obtained from the slope of the curve. The highest value for the diode activation potential—0.35V—was obtained after annealing followed by ion bombardment, and again no significant difference could be detected between tungsten and columbium. It was found that increase in contact force caused a drop in activation potential. A brief theoretical discussion suggests that correlation with contact area is doubtful at the small values of fractional hole current used.

Article by R. B. Allen & H. E. Farnsworth *J. Appl. Phys.* 27, May 1956 525-529

The Influence of Cathodic Sputtering in High Vacuum on the Rectifying Properties of Germanium

63/I

Germany. It is known that the rectifying properties of germanium vary appreciably with changes of its surface condition. In order to obtain more information on the behaviour of germanium in this respect pure germanium crystals were produced and their surfaces cleaned by a discharge in high vacuum. The crystals were grown

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under vacuum in an apparatus, details of which are given. The grown crystals were etched and tested singly by fitting them into a small socket which served as a cathode in a sputtering chamber. A thin wire whisker was employed as detector in the measurement of the rectifying effect. Special arrangements were made for the whisker to move accurately and thus facilitate measurements on a number of pre-determined detector points along the surface of the crystal. In the circumstances, the actual mechanism of discharge cleaning was more in the nature of an evaporation process than a cathodic sputtering process. After treatment lasting about 20 seconds a germanium layer could be observed on the walls of the glass container and the supply was switched off. Tests with the moveable whisker established that all rectifying properties of the crystal were lost at that stage. Subsequent tempering of the crystal in vacuum made no difference to this condition. But when tempering was carried out in the presence of oxygen at atmospheric pressure, the rectifying effect could be restored. Similarly, chemical or electrolytical etching of the crystal surface restored the rectifying properties of the crystal to those prior to discharge cleaning. It is concluded that the rectifying phenomenon depends on the presence of a 'defective' conductive layer on the surface of the germanium crystal which, in particular in the case where such layer contains oxygen, is removed during the sputtering treatment.

Article by H. Baldus *Z. Angew. Phys.* 6, June 1954 241-246

64/I

Properties of Selenium Rectifiers in the Presence of Various Impurity Centres

Germany. The life and performance characteristics of rectifiers depend on the purity of the selenium used initially and on the nature and concentration of additives. Rectifiers with a variety of added impurities were investigated and their characteristics recorded. The selenium used for the rectifiers was first chemically cleaned and then distilled at a pressure of 1 to 10 mm. Hg. The impurities were added before evaporating the selenium on to the carrier plates. The addition of bromine gave the best results. Tellurium and arsenic have a detrimental effect. In further tests selenium was used which was highly purified by fractional distillation in vacuum. Rectifiers made from this material were generally as good as commercial rectifiers made from so-called pearl-selenium with bromide additives. The effect of bromide additives on the characteristics of a rectifier made of highly purified selenium is less pronounced than in the case of commercial-grade selenium.

Article by F. Eckart & A. Schmidt *Ann. Phys.* 16, 1955 144-152

65/I

The Thermal Conductivity of Bismuth Telluride

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66/I

The Application of Vacuum Techniques to Certain Methods of Depositing and Melting Materials

See Abstract No.: 33/I

67/I

An Improved Method for the Production of Single Crystals of Semiconductor Materials

See Abstract No.: 137/I

68/I

Useful Impurities in Semiconductors and Phosphors

United Kingdom. In both semiconductors and phosphors a high degree of purity of the base material is required to enable the later addition of a controlled amount of impurity. Metals depend upon free electrons for their high conductivities, about 10^5 ohm. cm. units, whereas insulators are deficient in free electrons and have conductivities of the order of 10^{-13} ohm. cm. units. Crystalline insulators when in a pure state, have low values of conductivity if the crystal lattice is perfect. If certain types of impurity are present or if some disorder exists in the crystal the conductivity becomes higher. Materials such as silicon, germanium and indium antimonide have values of conductivity intermediate between those indicated above (Si $=10^{-5}$, Germanium $=10^{-2}$, Indium Antimonide $=50$, ohm. cm. units). These are the so called semiconductors. They are 'intrinsic' semiconductors because of their relatively high conductivities in a highly purified state. Some insulators may have their conductivity increased by crystal lattice disorders or by the presence of impurities. These are then 'extrinsic' semiconductors and conductivities lie between 10^{-6} and 10^3 ohm. cm. units. The increase in conductivity is due to either increased numbers of free electrons or of 'holes' which are able to move and carry current when a field is applied. Each atom of phosphorous added to silicon or germanium gives one extra current carrying electron whereas each added atom of aluminium gives an extra hole per atom. Less than one part in 10^7 of suitable impurity raises the conductivity of silicon from 1.5×10^{-5} to 0.2, of germanium from 0.015 to 0.6 and of zinc sulphide from 10^{-13} to 0.02 ohm. cm. units. Not all impurities have this effect although these may provide means of 'trapping' electrons or holes. The trapping effect decreases markedly with rise in temperature. The various applications of semiconductors (listed by the author) make it imperative that the conductivities are held within rather close limits. The crystals must therefore be prepared artificially. The transistor crystal, for example, has two junctions dividing the crystal into three zones, the central zone being well under 1/000 inch thick. In this zone, combination between electrons and holes must be kept at a minimum and great care must be taken therefore to avoid lattice defects which would lead to trapping or combination. By using chemical refining and zone refining for silicon or germanium, and by melting in vacuum or in the presence of an inert gas, large single crystals which are almost perfect can be grown. This is done by lowering a small perfectly formed crystal to the surface of the melt and slowly withdrawing it. Impurities may then be introduced by a surface alloying process,

for instance, applying a bead of indium to the germanium surface and heating it at 500°C. Germanium will then diffuse into the molten indium. Silcon diodes or triodes can be operated at higher power than germanium, but are more difficult to prepare. Phosphors depend on impurities for their luminescence, but if too much impurity is present the luminescent output falls. The presence of nickel or iron atoms may prove disastrous and the proportions of these materials must be below 1 part in 10^6. Many of the fundamentals of luminescence are not yet fully understood and control is incomplete. The use of 'light amplifiers' consisting of a combination of a photoconductive layer and a layer of electroluminescent powder is becoming more important and research is proceeding on these lines.

Article by D. A. Wright *Times Sci. Rev.* Autumn 1956 6-9

Grainless Phosphor Screens for T.V. Tubes and a Light Amplifier 69/I

United States. A luminescent coating deposited as a grainless layer avoids the diffusely scattered light associated with a conventional powder phosphor in television tubes. Such transparent phosphor screens of zinc sulphide can be made by a vapour-phase reaction as is described in the present article. With a screen of this kind, higher resolution and contrast are possible. Phosphor layers produced in this way also be may used as light-amplifying screens.

(*Author*)

Article by F. J. Studer *J.S.M.P.T.E.* 65, April 1956 197-200

Spectral Energy Distribution Curves of ZnS:Ag and ZnCdS:Ag after Thermal Vacuum Treatment 70/I

United States. Liquid settled screens of ZnS:Ag and of ZnCdS:Ag of thickness comparable to those of cathode ray tubes were subjected to various temperatures in vacuum. The temperatures ranged from 300° to 800°C and exposure times from 5 to 30 minutes. Spectral energy distribution curves were then obtained for these phosphors under electron bombardment. Intensity changes, colour shifts, and the appearance of new emission bands are noted. These seem to be related to the diffusion and evaporation rates of the phosphor components and the effects depend upon screen thickness as well as time and temperature of exposure.

(*Authors*)

Article by C. H. Bachman, M. L. Sawner & W. Allen *J. Electrochem. Soc.* 103, Feb. 1956 117-122

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Ultra-Violet Absorption of Atomic Nitrogen in Its Ionisation Continuum 71/I

See Abstract No.: 13/IV

New Krypton Light Source for the Vacuum Ultra-Violet 72/I

United States. The paper describes a source in which a molecular continuum of Kr is produced by microwave energy, giving a useful lamp for the range 1,250—1,850 Å. The body of the lamp consists of a Pyrex tube 10 mm. o.d., 5.5 mm. i.d., and 20 cm. long, closed at one end by a 1 mm. lithium fluoride window. The tube is attached to the spectrograph, with the window close to the slit, by a ground glass joint. The tube is pumped *via* a dry ice trap, and the discharge is excited by a microwave aerial placed entirely outside the tube. To prepare the lamp, it was pumped, outgassed by running with Ar at about 5 mm. Hg pressure, then pumped to 10^{-6} mm. and gettered by heating a Mg-BaAI getter in a quartz side tube. It was then filled with reagent-grade Kr to a pressure of about 190 mm. and the discharge started with a tesla coil. The life of the lamp is more than 50 hr. and is limited by increasing window absorption. A micro-photometer tracing is shown of the continuum, as photographed on a 21 ft.-vacuum spectrograph; this shows limits of about 1,255 and 1,650 Å. A table is given of the emission and adsorption lines reproduced below. As an example of the use of the lamp, a tracing

Atomic Lines Appearing in the Krypton Continuum and Useful as Wavelength Standards

Wavelength Å	*Intensity*	*Spectrum*	*Wavelength* Å	*Intensity*	*Spectrum*
1658.117	20	C 1	1329.590	40	C 1
1657.899	15	C 1	1329.108	40	C 1
1657.374	10	C 1	1328.836	15	C 1
1657.001	30	C 1	1306.036	25	C 1
1656.923	15	C 1	1304.872	30	C 1
1656.454	4	C 1	1302.173	30	C 1
1656.259	15	C 1	1295.597	ABS*	Xe 1
1654.055	5	C 1	1280.852	10	C 1
1561.433	20	C 1	1280.604	8	C 1
1561.339	5	C 1	1280.403	5	C 1
1560.687	15	C 1	1280.340	15	C 1
1560.301	2	C 1	1280.140	8	C 1
1494.673	10	N 1	1279.817	10	C 1
1492.624	15	N 1	1279.230	8	C 1
1481.760	30	C 1	1277.727	20	C 1
1469.640	ABS*	Xe 1	1277.551	50	C 1
1467.405	20	C 1	1277.282	40	C 1
1463.346	40	C 1			
1459.034	20	C 1			
1402.620	ABS*	Hg 1			

*Absorption lines. Wavelengths were determined against neighbouring lines.

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Article by P. G. Wilkinson *J. Opt. Soc. Amer.* 45, Dec. 1955 1044-1046

is also given of the absorption spectrum of benzene vapour, using the first order of the 21 ft-vacuum spectrograph. Some figures are given for the spectrum above 1,700 Å; this is very weak and it is suggested that the continuum could be photographed in the 4th order without overlapping. There is a very brief discussion of the theory of the Kr continuum, with suggestions as to the probable main transitions involved.

73/I

Light by Sylvania

United States. The Sylvania company is one of the American 'big three' lamp manufacturers who lead an industry which produced 1,079 million lamps of all types in the United States in 1955. Vacuum and compressed air systems are an indispensable part of the company's lamp making machinery. The lamp factories utilise compressed air at 100 p.s.i. supplied by large single and two-stage compressors, the latter having a capacity of 630 c.f.m., and also blower air at 4½ p.s.i. obtained from multiple blowers each with a capacity of 650 c.f.m. An important feature of the compressors is that they have non-lubricated cylinders and use graphite piston rings to produce oil-free air. Class E.S. Vacuum pumps rated at 26 inches of mercury supply general purpose vacuum, piped around the factories, and diffusion pumps produce the low pressures necessary for evacuating bulbs and fluorescent tubes. Processes which utilise compressed air include the formation of the bulbs, extrusion of the cement that attached the bulb to its base, the clean transfer and mixing of fluorescent and other powders, spraying, compressed air burners and directional flames used in shaping and sealing the bulbs. Compressed air is the motive power for a great variety of machines that lift and transfer materials and it is used for the protection of apparatus in automatic processes. An example of this is the safeguarding of the dies used to stamp bulbs with type and rating. A stream of compressed air is interrupted by the presence of a bulb on the production line. If, for any reason, there is no bulb on the line, then the undeflected air streams operate a catch which prevents the die from hitting the mechanism and being ruined. Vacuum does more than evacuate bulbs and tubes, although this is a major contribution. Bulbs are transferred by suction caps and vacuum is used to operate machinery. Some bulbs and tubes are partially silvered on the inside and pressures of 1 micron are maintained during this part of the process. The importance of vacuum to the Sylvania company is evident from a point made in speech by its president: 'Nature abhors a vacuum, but we love it! In fact, no small part of our success is due to the quality of our vacuum'.

Article by G. B. Richardson & R. James *Compr. Air Mag.* July 1956 199-203

74/I

Improvements r.t. Leak Detecting Apparatus for Use with Exhausting Machinery

United Kingdom. The patent is concerned with means for automatically detecting and isolating leaks in automatic apparatus for exhausting electric lamps and electron tubes. The method avoids false determinations due to pressure fluctuation in the exhaust lines. Furthermore, a leaking tube envelope is provided which is automatically isolated from the exhausting system of the machine so that air and contaminants are prevented from entering the system. The usual cycle of operation of exhausting machines with multiple exhaust ports provides for an indexing motion of the turret whereby successive steps in the cycle are produced at moments when the specific portions of a rotary vacuum valve register with each other. This rotary valve is arranged so that the envelope being evacuated is almost immediately advanced to a test position which is connected to the leak detector. The leak detector consists of opposed bellows which are exhausted to the same degree as the vacuum tube or electric lamp. If these bellows are at the same pressure, a connection block between them is maintained in an equilibrium position. The connections necessary are only maintained long enough to bring the lamp and the bellows to the same pressure. The next step in the operation of the leak detector occurs when the exhaust branch is sealed from all parts of the apparatus by the operation of a magnetic vacuum valve and, furthermore, a second magnetic valve is operated to isolate one member of the pair of bellows from the other to which the lamp is connected. These operations are effected by the rotation of cams on the main cam shaft of the exhaust machine. The result is that one of the bellows is kept at the original exhaust pressure, whereas the other, together with the exhaust lines to the lamp, are subject to pressure variation if air leaks into the lamp. If the lamp does not leak, no further operations will occur until the lamp and the associated exhaust port are about to be indexed away from the station. On the other hand, if the lamp is leaky, it produces a pressure increase in the bellows connected to it with the result that these bellows expand towards the other member of the pair, which still remains in the original exhausted condition. The connection block between the bellows therefore moves. The response effected by the movement of this connection block is proportional to the leak. Moreover, as both bellows and the lamp were originally exhausted together, pressure fluctuations in the exhaust apparatus are balanced. The displacement of the connection block operates a switch which causes a warning lamp to light up and also operates a mechanism which closes the pinch-clamp to the leaky lamp concerned. The leaky lamp is therefore automatically sealed off from the vacuum system. This closed position is maintained throughout the following steps in the exhaust cycle.

British Thomson-Houston Co. Ltd. *Brit. Pat.* 753,185

75/I

Improvements i.o.r.t. Bulb Washing and Reflector Coating Apparatus

United Kingdom. Bulbs which are to be coated inside with metal by vacuum evaporation to give a reflecting surface must be clean, dry and free of all foreign matter before evaporation, if a satisfactory coating is to be obtained. The practice has been to wash them, with chemically pure water for instance, and allow them to thoroughly air dry by prolonged storage in a neck-downward position. However, they are liable to become contaminated again during this storage period so a method, to which this patent applies, has been devised to eliminate this and make cleaning and metallising one automatically controlled process. Bulbs with their necks downwards, are fed either by hand or automatically on to one of two horizontal circular 16-head carriers which

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are indexed, in step, in an anti-clockwise direction to bring each work station to the loading point. An automatic loader may be used to lift bulbs from a feed conveyor, gripping them by applying a suction pad to their top and rotating and lowering them on to the first station of the cleaning carrier. A second suction pad, attached to the same loader, transfers, at the same time, a bulb, which has completed the cleaning circuit and returned to the first station of the cleaning carrier, to the second station of the coating carrier. The bulb is located on the cleaning carrier over an axial hole by three spring feelers projecting inside the neck. The heads are rotated at all but the 1st, 6th and 7th stations. At the second station a spray of cleaning agent such as de-ionised water at 135°F is directed from below into the bulb. At the 3rd, 4th and 5th stations the water is allowed to drain from the bulb, assisted by high pressure air jets. A final natural drainage period is allowed at the 6th and 7th stations, before radiant gas heaters, located at the 8th and 13th stations, heat the bulb to vaporise the remaining water. During the last three stations the bulbs pass through a travelling oven which raises them to a temperature just below their softening point. As soon as the bulbs return to the first station, they are removed and, as has already been described, transferred to the second station of the coating carrier. Here the bulb is lowered over a holder which forms the vacuum connection. An arm is lowered on to the top of the bulb to hold it in position and a lever-operated expanding rubber sealing-ring is made to seal the bulb to the holder as the head moves to the 3rd station. A vaporiser element, plated with the metal to be used for coating is manually fitted to the head at the first station. Each head is equipped with a mercury diffusion pump and Pirani gauge. The backing line of the pump and gas-inlet line to the head are lead to a rotary valve at the centre of the carrier. A rough vacuum pump is connected by this valve to each head from station 3 onwards to pump the bulb *via* the mercury diffusion pump. At station 5, stationary contacts communicate with moving contacts on the head to connect the Pirani gauge to a relay circuit which, if the pressure is low enough, causes the vaporiser filament to be heated at the next station. If the pressure is not low enough the bulb is not coated during that revolution of carrier. At station 7 to 13 the deposition of metal is carried out with the filament being run at a higher temperature at each station. Between the 13th and 14th stations an inert gas, such as a mixture of hydrogen and nitrogen known as 'forming gas' is admitted to the bulb and pumping is discontinued. The bulb and vaporiser element are allowed to cool at station 15. The completed bulb is unclamped from the head as it moves to station 16, where it is manually removed.

British Thomson-Houston Co. Ltd. *Brit. Pat.* 746,668

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Method for the Manufacture of Plastic Articles Having Reflecting Surfaces Thereon

76/I

United States. This invention refers to a method of metallising plastic photoflash reflectors, car door handles, etc. A cullulose acetate butyrate base of the desired shape is first covered with a thin layer of a ura-formaldehyde resin by dipping; the latter is caused to adhere by baking for ½–2 hours at 160–180°F. This coating serves to prevent outgassing of the plastic base during subsequent vacuum coating which would otherwise prevent satisfactory deposition. The metal layer—usually aluminium—is then deposited on the article by conventional vacuum evaporation techniques. The metal surface is protected by a transparent coating of epoxide-urea resin produced by dipping followed by baking; on top of this coat a silicone resin layer is placed as a further protection, produced by dipping and air drying. Details are given of the various dipping solutions used.

G. Meyer & Eastman Kodak Co. *U.S. Pat.* 2,699,402

Improvements in Metal-Coated Recording Strips

77/I

Germany. Reference is made to earlier patents (Nos. 710, 411 and 708, 912) describing a method to be used in recorders, whereby a trace is burnt out in a metal coating covering the recorder strip (of insulating material) by passing an electrical current through a stylus. The present specification deals with the nature and properties of the metal coating covering the strip. If the metal coating is too thick, a high current is needed to burn it out. This results in a wide fringed furrow rather than a clean trace and in charring of the insulating substrate. To overcome the difficulty the coating should have a comparatively high resistance, preferably 4 to 10 ohms per square and should be prepared from a metal of high durability. *E.g.*, zinc, 0.1 μ thick, would be suitable but is liable to early disintegration in air. Aluminium forms oxide films which adversely affect the conductivity. However, nickel layers, which are specified in the patent, are satisfactory. Layers 0.05 μ thick having the appropriate resistance may be produced by vacuum evaporation, cathode sputtering or the thermal decomposition of nickel carbonyl.

Robert Bosch G.m.b.H. *Brit. Pat.* 752.254

Method of Making Electrical Capacitors

78/I

See Abstract No.: 52/III

Drying Transformers

79/I

Czechoslovakia. It is well known that the drying of large transformers, involving as it does a number of very different materials, is facilitated by vacuum processing. However, a very high vacuum is not necessarily the speediest. V. Hrbek, V. Zita and B. Paderta have investigated the relations between temperature and pressure and evolved a method which reduces the drying period by about one-third of its previous duration. The insulation resistances can be increased to 5,000 MΩ and the loss factor reduced to 1% at 20°C.

Abstract by Anon. *Elect. Rev.* 28.10.1955

Abstract No. and References

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80/I

The Operation and Maintenance of Hydrogen-Cooled Generators I.

United Kingdom. More than sixty turbo-generators using hydrogen instead of air-cooling have been commissioned in power stations of the Central Electricity Authority since the first was installed in 1949. The relevant characteristics of hydrogen as a cooling medium, compared with air are given in a table reproduced below.

Relevant Characteristics of Hydrogen as a Cooling Medium Related to Air as Unity, at N.T.P.

Characteristic	*Air*	*Hydrogen*
Density	1	0.0696
Specific Heat iconst. pressure	1	14.35
Heat Capacity	1	0.996
Thermal Conductivity	1	6.69
Heat Transfer	1	1.51

Tests have confirmed that hydrogen at atmospheric pressure is 0.8% more efficient than air and the smaller volume of gas required enables great reduction in fan size etc. Further, since the windage losses are so small the new system can be operated at 15 or 30 lb. p. sq. inch above atmospheric pressure. This permits considerable increases in specific output. Since hydrogen is inflammable, the purity of the gas used is normally in excess of 95% and the air is first expelled from the casing before admitting hydrogen. Thereafter, an excess pressure of hydrogen above atmospheric is always maintained in order to prevent any air leakage into the system. To ensure a gas tight-enclosure with minimum leakage the hydrogen-cooled generator is mounted within a heavy fabricated steel casing. Heavy end shields enclose the ends of the machine and, in some cases, provide mountings for the rotor bearings. Ring or axial, and thrust or radial types of oil seals are used as shaft seals to maintain effective separation between air and hydrogen. These seals all depend on the formation of a barrier of oil under pressure between a stationary and a rotating surface. The design and operation of each type of seal is discussed and their requirements are compared. It is usual to vacuum-treat the oil before admitting it to the floating ring type of seal since oil-carrying air would cause contamination of the hydrogen and replacement of the gas would become expensive. Seals of the thrust type introduce much less air and no outgassing of the feed oil is necessary. A diagram of an seal oil system with vacuum treatment is given. The seal oil passes through a tank held at a pressure of about $\frac{1}{2}$ mm. Hg by a rotary pump. The oil enters through a set of nozzles which break it up into a fine spray thus assisting the gas removal. An oil pump draws oil from the bottom of this tank and pumps it to the seals *via* a cooler. The oil pump has a higher capacity than that needed to supply the seals and the excess is returned to the vacuum tank *via* a second set of nozzles directed downwards on to the oil surface to burst any bubbles present as foam. Precautions are taken to see that oil is always supplied even if both the oil and the vacuum pump become inoperative.

Article by F. R. L. Creek *Steam Engr.* September 1956 378-383

81/I

Article by T. Sato, S. Nagao & Y. Toriyama *Brit. J. Appl. Phys.* 7, Aug. 1956 297-298

Space-Charge Limited Current in Insulating Oil

Japan. The current-voltage characteristics for a vacuum tube containing insulating oil was measured. The tube was mounted vertically, with oil surrounding the plane horizontal anode at the bottom, and a tungsten filament at the top. The characteristics were plotted with various depths of oil above the anode, and the results indicate space-charge limited conduction by negative ions. The characteristics fit a theoretical law well, and give a value for the (negative) ionic mobility $\mu = 0.6 - 1.1 \times 10^{-4}$ cm./s. per V/cm. This agrees with values obtained by previous workers using a different method.

82/I

Electron Bombardment in Thin Dielectric Layers

United Kingdom. To investigate dielectric layers of Pyrex, arsenic sulphide, antimony sulphide and mica under bombardment with electrons of energies up to 50 keV, a magnetically focused electron beam was directed on to the dielectric which was between 0.7 and 4 μ thick and sandwiched between vacuum deposited aluminium electrodes (about 3×10^{-6} cm. thick) which were practically transparent to the electron beam. An arrangement of auxiliary electrodes containing apertures around the dielectric layer has the function of ensuring that the measured total incident electron current i_p included only electrons absorbed and transmitted by the dielectric specimen. The electrons transmitted were collected in an aluminium tube and the collector current i_c recorded. An electric field E was produced across the specimen dielectric when required by applying a bias potential between the aluminium electrodes. Dielectric films of Pyrex about 1 μ thick were obtained from blown bulbs; mica films not less than 4 μ thick could be obtained by cleavage. Vacuum deposited films of arsenic sulphide and antimony sulphide were formed (see *J. Sci. Instrum.*, **32**, 1955, 34) together with the aluminium film electrodes on thin electrolytically polished copper foil. The specimen was then mounted in a mica frame and a drop of nitric acid applied to remove the copper quickly. Preliminary tests were made on an evaporated aluminium foil (0.316 mg. cm^{-2}); i_c/i_p was plotted against V_p, the energy of the primary incident electrons. Extrapolation of the linear portion of this graph to i_c/i_p lead to a value $V_p = V_o$. Results were in agreement with the Thomson-Whiddington law:

$$V_p^2 - V_x^2 = b\rho x$$

where V_x is the energy the electrons possess at a depth x within the foil, ρ the density and $b = V_o^2/m$, m is the mass per unit area of the foil. For films of dielectric with both aluminium electrodes at the same potential electron currents were found to flow to the bottom electrode before any of the incident electrons had sufficient, energy to penetrate the dielectric. Results suggest that this is a general property of dielectric films under

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electron bombardment. Analysis of results shows that a steady current of slow electrons flowed in a bombarded dielectric film if the primary beam had penetrated to about half the depth of the specimen. Experimental values of primary and secondary currents for specimens of different thicknesses fall on common curves when plotted against $(V_p/V_0)^2$ as the independent variable. For mica and Pyrex the current distribution is given for applied fields of up to 10^6V cm^{-1}. Curves obtained are similar to those given by Ansbacher and Ehrenberg (*Proc. Phys. Soc. A*, 1951, **64**, 362) except that the current gains are considerably lower. The secondary current curves are interpreted in terms of the displacement of change carriers in the space-charge field within the dielectric.

Article by W. E. Spear *Proc. Phys. Soc.* **68B**, Dec. 1955 991-1000

On the Measurement of Electric Constants of Thin Metallic Films 83/I

See Abstract No.: 50/III

Improvements i.o.r.t. the Formation of Metallic Films on Articles by Thermal Evaporation 84/I

See Abstract No.: 16/III

14 — MECHANICAL SCIENCES — 14

Utilising Plastic Impregnation in Equipment for Nuclear Research 85/I

See Abstract No.: 82/II

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Save Time in Vacuum Vessel Design 86/I

United States. The 1952 edition of the A.S.M.E. Unfired Pressure Vessel Code included a chart for determining the necessary thickness for the walls of spherical and cylindrical vessels subjected to external pressure. Use of this chart involves a trial and error procedure. A new chart has been designed to be direct-reading without a trial and error stage by standardising on one external pressure of 15 p.s.i. The chart can be used to determine the wall thickness of cylindrical and spherical vessels and those of ellipsoidal, hemispherical and torispherical heads when the material is carbon steel with a specified yield strength of 24,000 to 30,000 p.s.i. For every case simple formulae are given which enable the chart to be used once the dimensions and maximum working temperature of the vessel have been fixed.

Article by J. A. Hunter *Petrol. Ref.* **34**, Feb. 1955 100.102

Aluminium Foil Rupture Discs Offer Low-Cost Protection 87/I

United States. Discs of aluminium foil clamped between pipe flanges have been tested in pressure tanks to determine the pressure at which they burst and the type of deformation that occurs under pressure. It is thought that foil discs should be suitable as rupture discs in processes where very frequent rupture is expected. They would be cheaper than the rupture discs of aluminium sheet which are commercially available. These are used in the chemical and refining industries to replace safety or relief valves where highly corrosive conditions exist or where quick pressure relief is required. Experimental diaphragms were prepared from commercial 2S aluminium alloy foil in two tempers, 2S-0 (dead soft) and 2S-H 18, and in thicknesses from 0.001–0.010 inch. Three pressure test tanks of diameters 6 inch., 4 inch. and 2 inch. respectively were used. The pressure in the tank was measured by a Bourdon-tube vacuum and pressure gauge equipped with an auxiliary hand to indicate the maximum pressure reached. A Rutishauser pressure pick-up connected to an oscilloscope was installed immediately below the rupture disc. The trace on the oscilloscope screen was photographed to obtain a record of the variation of pressure with time. Starting from atmospheric pressure discs were subjected (*a*) to a gradual increase of pressure until bursting took place, and (*b*) to impact loading, *i.e.* a sudden increase of pressure which was varied until the lowest bursting pressure was obtained. These two tests were repeated on discs which were first subjected to vacuum preloading by evacuating the test tank to 27–29 inch. Hg before applying pressure increases to the discs. Some of the results obtained in the experiments are listed below. The rupture discs

Tank Size (nominal) (in.)	*Rupture Disc thickness (in.)*	*Temper*	*Bursting Pressure (lb./sq.inch gauge).*			
			Gradual Load		*Impact Load*	
			from 1 atm.	*from vacuum*	*from 1 atm.*	*from vacuum*
2	0.001	0	4	—	—	—
		H-18	13	—	—	—
	0.005	0	64	66	63	62
	0.005	0	31	32	32	32
		H-18	48	47	46	34
	0.010	0	83	83	83	80
6	0.001	0	1	—	—	—
		H-18	3			
	0.005	0	22	23	20	20
		H-18	30	35	28	28
	0.010	0	57	57	57	53

tested without vacuum preloading burst at a similar pressure under both gradual and impact loading. In the case of half the S-0 specimens vacuum-preloading appeared to lower the bursting pressure under impact loading. The H-18 discs showed a similar trend. In general the soft discs burst at a lower pressure than harder discs of the same thickness treated in the same way. This did no apply, however, in the case of 0.003-inch. material. The oscilloscope records show that a pressure build-up takes place in 20-30 msec. An almost instantaneous pressure relief occurs as the disc bursts and there follows a period of rapid but relatively minor pressure oscillations as the tank pressure approaches atmospheric. Photographs of the discs show that they deform spherically under pressure. Photographs of the bursting process were taken with a 16-mm. Fastex camera and show the initial deformation, the development of tears and the final bursting of the whole disc. The results obtained on the deformation of the discs are compared with the findings of workers on the deformation of structures such as ships' hulls by underwater explosions.

Article by
P. B. Stewart
& R. T. Fox, Jr.
Chem. Engng. Progr.
52, March 1956
115M-120M

88/I

High-Temperature Brazing

United States. Brazing as a technique has been known for a long time but it is only within the last two decades that it has been widely used in industry. Recent developments promise even wider applications. In brazing, a non-ferrous filler metal of lower melting point than that of the metal parts being joined, and which 'wets' the base metal, is melted into a well-fitted joint, being drawn in by capillary action. True brazing takes place at 800°F or above, any similar joining technique at lower temperatures is soldering. The present article refers to processes using filler metals that melt above 1,600°F and where the brazed joint is subjected to temperatures of 1,000°F, or above. Since inter-diffusion between the base metal and the filler metal often raises the melting point of the filler metal itself, brazed assemblies can often be used at temperatures higher than the actual brazing temperature. The development of exceptionally dry hydrogen furnace atmospheres was largely responsible for the successful application of high-temperatures brazing as, under these conditions, brazed assemblies can be produced without fluxes. Fluxes present a cleaning problem and there is the danger of weak joints due to entrapped flux. When joining metals susceptible to gas contamination such as titanium and zirconium, inert gases can be used, or the improved modern vacuum techniques, which eliminate contamination by furnace atmospheres. Diffusion bonding and diffusion brazing, though not strictly brazing techniques as such, employ the same design requirements, joint preparation and furnace technique and need to be considered whenever the advantages of brazing are desired. Among the most common brazing-filler metals are copper and nickel-base alloys; with many of the latter the strength of the brazed joint equals that of the base metal. Among others, a silver-manganese alloy is used chiefly with stainless steel, and a number of palladium alloys have been used for special high temperature applications. Of the pure metals used as filler metals, molybdenum, rhodium, gold and nickel are relatively common. With these bonding occurs as the result of different mechanisms depending on the relative melting points of the filler and the base metal, and whether or not inter-diffusion results in the formation of a low-melting alloy. Many problems remain, for instance high-temperature brazing would be simplified and the problem of atmospheres might become less important if methods were available for pre-plating with the rather complex filler alloys, either as alloys, or in controlled layers of the various elements.

Article by
R. M. Evans
Battelle Tech. Rev.
5, August 1956
8-12

89/I

Brazing in a Vacuum

United States. Two processes are covered by this term: True 'vacuum brazing', in which purging and brazing are completed *in vacuo* and 'vacuum purge atmosphere brazing' which uses an hydrogen atmosphere for the actual brazing. In both processes the vacuum purge is performed in a vacuum furnace at 500°C. Purging is regarded as complete when a pressure of 30 microns Hg is reached. This normally takes 15 minutes. When brazing is carried out in hydrogen, the same furnace is used, at temperatures of 1,700°F and 2,100°F, with the gas at a slightly positive pressure. Vacuum purging has several advantages such as (*1*) considerable time saving; (*2*) economic use of gas (one retort volume) and (*3*) better quality joints. True 'vacuum brazing' possesses the additional advantage of being less hazardous as no hydrogen is used. Degassing occurs and this gives definite bonding and strength improvements to vacuum brazed joints. Most brazing materials except those with volatile components (e.g. Cd, Zn) can be used. Furnaces for vacuum brazing are of a special design to allow for high temperature operation: Double-pumped furnaces with the furnace shell containing the heating elements held under a rough vacuum to reduce pressure differentials are employed. Pressures during vacuum brazing are kept under 1 micron Hg. A high-speed fractionating oil diffusion pump, suitably backed, is normally used. This is capable of maintaining a vacuum of 0.001 micron Hg during the cooling period until the vacuum is broken at about 300–400°F. Such a vacuum brazing furnace is equally suited to degassing and annealing processes.

Article by
J. H. Newitt
Steel
4.6.1956
107-108

90/I

Preliminary Investigation of Properties of High Temperature Brazed Joints Processed in Vacuum or in Molten Salt

United States. The investigation described was carried out to evaluate the effects of temperature and time variations for both molten-salt and vacuum brazing. Also investigated were the effects of nickel additions to the brazing material used (Nicrobraz) and a protective coating for the specimen when brazed in the molten salt-bath furnace. A series of practical experiments capable of statistical analyses are described together with the resistance-heated vacuum furnace and induction-heated molten barium-chloride salt bath furnace, in which the various test specimens were processed. The details of the various designs and materials of the test specimens employed are given. The tests showed that the vacuum and molten salt bath processes are capable

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of producing brazed joints with shear strengths of the order of 63,000 and 48,000 p.s.i. respectively under proper conditions and that the average shear strengths of joints brazed in the molten salt bath increased approximately 18% with an increase in the brazing temperature from 2,000° to 2,150°F. The strengths of the vacuum brazed joints were found to be a function of temperature and time at given temperature, the strongest joints, in the order of 63,000 p.s.i., being produced by brazing at 2,075°F for 15 mins. It is reported that the addition of nickel to the Nicrobraz alloys produced only a slight improvement in the shear strength of the salt-brazed specimens and had no effect on the shear strength of the vacuum-brazed specimens, while the protective coating developed during the tests increased the shear strength of joints processed in the molten salt bath by a considerable amount.

Report by C. A. Gyorgak & A. C. Francisco *N.A.C.A. Rep.* TN.3450 May 1955

High-Vacuum Brazing

91/I

United States. Vacuum brazing is being used in assembling jet-engine parts. The work is mounted on a base and surrounded with brazing wire, and a double-walled bell-jar is lowered over it and sealed by means of water-cooled 'O'-rings. The space between the walls contains heating coils and both that space and the chamber interior can be evacuated. At 2,150°F the brazing wire melts and bonds the parts. The same time is required as for dry hydrogen-brazing (1½ days), but it is reported that the vacuum method is 50% superior.

Note by Anon. *Compr. Air Mag.* May 1956

Good Control Makes Titanium Welding a Shop Tool

92/I

United States. The results of an extensive test programme on the mass-production welding of titanium carried out by the Westinghouse Electric Corp. are reported, and the conditions necessary for the satisfactory welding of titanium are indicated. Atmospheric contamination must be avoided. This is the main factor governing the welding problem. The best method is undoubtedly inert gas tungsten arc welding. Flash-welding is satisfactory if carefully controlled, but resistance-welding gives joints with poor properties. Brazing with various filler metals may be carried out under meticulous control, especially in vacuum. Arc-welding, in particular, requires the protection of the hot metal from atmospheric contamination. Moreover, oxide films should be removed before welding, but the small amounts of water vapour present do not appear to have any detrimental effect. Protection from the atmosphere in arc welding is given by a blanket of argon, helium or a mixture of both. If convenient, this may be achieved by the use of a collapsible chamber which is purged by filling with inert gas a number of times, being emptied by collapsing after each filling. Open welding may be achieved by manual or automatic means as long as a blanket of inert gas is provided *via* an oversize nozzle, or using a trailer nozzle behind or around the torch nozzle. Inert gas should flow through an oversize nozzle at about 12 cph, but in all cases too great a flow of gas may introduce air through turbulence, and must be guarded against. A proper back-up fixture should be employed to control warpage, with inert gas feeds through manifolds in the back-up to the underside of the weld. Currents used for titanium welding are up to 50% greater than for steel, partly due to the low thermal conductivity of titanium. Direct current gives the best results. In manual welding, as short an arc as possible is desirable, and no harm results if the tungsten electrode touches the work. In joints thicker than 0.9 inch moving the arc ahead ¾ inch and then back ½ inch, produces a sound joint. Rapid torch motion may produce turbulence and is to be avoided. The weld should be immediately chilled when complete, to lessen contamination and distortion.

Article by F. D. Seaman *Iron Age* May 1956 64-66

Leak Testing of Type-347 Stainless Steel Welds

93/I

United States. A problem which occurs in designing liquid-metal-heat transfer components to operate with a positive inert gas pressure to protect the liquid from contamination is, just how thick must a weld be to provide a gas tight joint? Four different 347 stainless steel specimens, differing in ferrite content were used in the experiments. They were:

Material	*Ferrite %*
Arcos E 7458	7%
,, ,, 8109	4% (Titania coated)
,, ,, 7460	2%
,, ,, 7478	0%

Each sample was machined in the shape of a stepped pad 3 inch. × 4½ inch. with steps of 0.030 inch, 0.050 inch, and 0.075 inch thickness. The mass spectrometer leak testing method was used. Details of the experimental procedure are given. Leakage rates for periods of 30 mins. at standard atmospheric temperature and pressure were recorded as follows:

Material	*Leak Rate*
Arcos E 7458	64×10^{-6} c.c./sec.
,, ,, 8109	NIL
,, ,, 7460	NIL
,, ,, 7478	56×10^{-6} c.c./sec.

Using a pin-point helium probe, the leaks were found to be in the 0.050 inch step in each case and were due to the presence of slag inclusions. This was confirmed using a red dye penetrations method and by radiograph. The leak rates recorded were in excess of the tolerance figure of 0.05×10^{-6} c.c./sec. as prescribed for S.I.R. Mark A sodium pipe welds but in all cases it was found that a sound weld 0.030 inch or more in thickness was leak-tight over the test period of 30 mins.

Report by W. L. Fleischmann & A. J. Herd *A.E.C. Rep.* KAPL-M-AJH-2 October 1955

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15 — PHYSICS — 15

94/I

The Velocity of Light

United Kingdom. The various methods used from the 17th century to the present day for measuring the velocity of light are reviewed and their accuracy is discussed. Up to 1941 an average figure, obtained from different experiments of 299,776±4 km/s with an experimental scatter of about 100 km/s was considered adequate. Since then a more closely defined value has been required. Some of the values obtained in modern experiments are quoted below. In 1946 a cavity resonator, was used to determine the velocity of electromagnetic radiation. Knowing the dimensions of the resonator and the frequency at which resonance occurs, the velocity can be determined. Effects due to the refractive index of air can be eliminated by operating the resonator in vacuum. By using a range of oscillator frequencies and varying the dimensions of the cavity it is possible to eliminate end effects, resonator diameter and wall resistance from the calculations. In the Michelson interferometer method radio waves of known frequency are directed down a waveguide to a junction where they are split into two equal beams. One beam is radiated into open air and a portion is returned from a distant reflector to the junction and a detector. The other beam is contained within a waveguide network and is reflected back to the junction and the detector after being attenuated to the same extent as the beam in air. The two beams are combined at the detector. The intensity of the signal depends on the relative phases of the two beams and passes through a maximum and minimum as the reflector is moved through half a wavelength. The geodimeter, an instrument used for surveying, has been used for optical measurements of light velocity. A parallel beam of light waves, modulated at a frequency of 10 Mc/s by a Kerr cell, is reflected back from a mirror at a distance of about 10 Km. The reflected wave is detected by a photomultiplier tube, the sensitivity of which is varied at the modulation frequency. The strength of the detected signal depends on the phase of the returning wave and hence on the distance travelled. The Shoran radar system has also been used for velocity determinations. In this method an aeroplane flies over the line joining two transmitting stations which are a known distance apart. The time interval between the pulses received from the two stations is noted on a cathode ray screen. A recent method is based on the determination of the molecular constants of hydrogen cyanide by both optical and microwave spectroscopy. The results in one case are expressed in wavelength units and in the other in frequency units; by combining the two the velocity of light can be obtained. Modern experiments have not shown any variation of the velocity of light with time or the frequency of the radiation. From the results available the author concludes that the most probable value of the velocity is 299,793±0.5 km/s.

Results of Recent Determinations of the Velocity of Light (c_0)

Date	*Author*	*Method*	*Result (km/s)*	*Experimental scatter (km/s)*
1950	Essen	Cavity resonator	200 792.5±1	1.5 (including systematic effects)
1951	Bergstrand	Optical, Kerr cell geodimeter	299 793.1±0.2	5
1951	Aslakson	Radar	299 794.2±1.9	13.5
1954	Froome	Radio interferometer	299 793.0±0.3	0.7
1954	Plyler	Spectral lines	299 792 ±6	*

*Result obtained by a least squares analysis of the observations.

Article by L. Essen *Endeavour* 15, April 1956 87-91

95/I

Energy Absorbed in Solid Thin Layers

France. Assuming, as a first approximation, that a thin film can be treated as a continuous medium which is homogeneous, isotropic and the two end surfaces of which are plain and parallel to each other, the authors have calculated the proportion of incident luminous energy and the proportion of luminous energy having effectively penetrated into the layer and been absorbed by it. The results are obtained in terms of the parameters normally employed to indicate the characteristics of the film in question such as optical thickness, refractive index and extinction coefficient. The theoretical study has produced certain results inconsistent with the assumptions made and this has been qualitatively confirmed by practical measurements taken by the authors on vacuum evaporated gold and silver films.

Article by P. Rouard, D. Male & J. Trompette *J. Phys. Radium* 17, June 1956 466-471

96/I

Study of the Optical Constants of Thin Gold Films

France. The optical constants determined by Goos (*Z. Phys.* **106**, 1937, 606) in the region 265–1050 mμ for thin gold films of a thickness of 10.4 Å to 1080 Å are used as basis for the determination of the constants reported in the present article by the author. The differences between the values of the optical constants for thin films and for the bulk metal are considered to stem from a progressive reduction of the influence of the resonant frequency characterising the bulk gold, as film thickness decreases. The frequency expressed in wavelengths per cm. equals 18,000.

Article by F. Grard *J. Phys. Radium* 17, May 1956 414-419

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A Study of Transparent Highly Conducting Gold Films

97/I

United Kingdom. During the development of electrically conducting transparent coatings on aircraft windows for the purpose of de-icing by resistance-heating, gold films, sputtered on to bismuth-oxide base layers on glass, were found to give excellent results, and have been studied in detail. Gold was sputtered in argon gas (99.8% pure), and bismuth oxide was sputtered in argon-air mixtures, sufficient air being introduced to ensure a clear oxide film. Film thickness of gold was measured by colormetric estimation and by weighing. The thickness of bismuth oxide was estimated by optical methods, exact measurement not being required. Using a current density of 1.5 mA/sq.cm. on pre-cleaned cathodes, the sputtering rate of gold was 11 Å per sec. and of bismuth oxide, 6.7 Å per sec. The optimum values of conductivity and optical transparency were obtained by 'sandwiching' a 100 Å-gold film between two bismuth oxide layers, so that the total optical thickness corresponded to a high-index half-wave layer with maximum mid-band transmission. After annealing at 350°C for a few minutes, the resistance of the film was only 4 ohms per square for an optical transmission of 82%. Heat treatment was also possible at 450°C, when further reduction in resistance was obtained, lowering the specific resistance of the gold almost to its bulk value. The effects of annealing and variation of electrical resistivity with thickness were studied. A graph shows the resistivity of annealed and unannealed films plotted against film thickness at 200°C at room temperature and at −183°C. Bulk values are also shown, and it can be seen that annealed films approach closely the bulk material for films thicker than about 200 Å. The results are discussed in terms of the theory of electron scattering in thin layers. It is concluded that after annealing, the gold film, in which surface-tension has been reduced by the presence of the bismuth oxide layers, is composed of large lateral monocrystals, in which condition, the scattering of conduction electrons at the film boundaries is almost specular. The optical constants of the composite films were calculated from measurements of reflection and transmission and thickness. Phase change on reflection and transmission was also measured. The effect of the glass base was allowed for, and the optical properties of three high conductivity gold films are given in a table, reproduced below. The real and imaginary parts of the complex refractive index are given together

Optical Properties of three High-Conductivity Gold Films

Film Thickness (mass/area basis) (*A*)	*Film Resistivity PF* (*ohm cm*)	*Wavelength* ($m\mu$)	*Transmission and Reflection Factors* T	R_1	R_2	*Optical Constants* ν	k
39	17.2×10^{-6}	436	0.643	0.192	0.134	2.13	1.46
		481	0.605	0.155	0.099	1.78	1.55
		546	0.776	0.104	0.057	1.29	2.10
		636	0.803	0.075	0.021	0.93	3.01
71	6.7×10^{-6}	436	0.583	0.177	0.091	1.80	1.66
		481	0.663	0.138	0.060	1.44	1.70
		546	0.785	0.075	0.017	0.68	2.41
		636	0.829	0.062	0.014	0.43	3.06
103	5.6×10^{-6}	436	0.524	0.174	0.074	1.79	1.61
		481	0.617	0.133	0.039	1.42	1.58
		546	0.763	0.071	0.002	0.64	2.14
		636	0.770	0.113	0.060	0.30	3.38

with the reflection coefficients from which they have been calculated. Electron micrographs and diffraction patterns were taken from several specimens, and some have been reproduced. The diffraction patterns studied show the gold crystallites to vary in diameter from about 50 Å up to 1,000 Å. Bismuth oxide began to crystallise after heating to 450°C. The micrographs show that the high-conductivity films on the oxide substrate have a more continuous structure than the gold films deposited directly on to glass. There is sufficient evidence to conclude that the gold crystallites in the high-conductivity films are probably monocrystalline lamellae of diameter up to ten times the film thickness. An appendix gives the basis of the optical calculation using the 4-terminal network theory.

Article by E. J. Gillham, J. S. Preston & B. E. Williams *Philos. Mag.* **46**, Oct. 1955 1051-1068

On the Reflection and Transmission of Light through Thin Transparent Films

98/I

Czechoslovakia. In this paper a formula is deduced for the reflection and transmission of light through one thin film using Fresnel amplitudes which are orientated according to the direction of the passage of the rays of light. In this method no assumptions are made and a formula is obtained which is more general than that used normally. This formula is then used as the starting point for the deduction of formulae for the reflection and transmission of light through two or more thin films. An explanation is given of the complication of the formula when the reflection of light from the upper film, adjacent to the air, is computed. The auxiliary phase, deduced by the author in a previous paper, is also explained as a necessary consequence.

Article by A. Vasicek *Czechosl. J. Phys.* **6**, August 1956 341-348

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99/I

Filmed Surfaces for Reflecting Optics

United States. Front surface mirrors are used today in many optical and most infra-red optical devices. To keep the energy losses due to reflectance in an instrument low, it is important to know the reflectance of all mirror metals over a wide spectral region. The reflectance of aluminium, silver, gold, copper and rhodium, the most important mirror metals, has been measured when freshly prepared as vacuum evaporated films. The reflectance depends on the pressure during evaporation, the rate and angle of evaporation of the metal, the thickness of the coating and ageing of the film. It is shown graphically that the reflection of aluminium is increased by evaporating at lower pressures and high rates of evaporation. Aluminium films evaporated in 250 sec. had 76% less reflectance in the ultra-violet, 10% less in the visible and 1% less at 10μ in the infra-red than films evaporated in 7 secs. Tables are given for the fall in reflectance through ageing in air and under the influence of ultra-violet light. Films produced from extremely pure aluminium had higher reflectance and corrosion resistance than those from commercially pure (99.5%) metal. Surface coatings can be used to protect the aluminium and enhance the reflectance. Magnesium fluoride has been used, but does not give sufficient chemical protection and only forms a hard film when evaporated on to substrates kept at 250–300°C. Silicon monoxide is especially suitable. The properties of films of this material depend strongly on the evaporation conditions and highly oxidised films formed by slow evaporation at 1×10^{-4} mm. Hg are best. Though the material has an absorption band at 10 μ, the effect of this on the reflectance of a coated mirror is slight. An explanation is given of this phenomenon. Multiple layer films, such as Al_2O_3—TiO_2 and MgF_2—CeO_2 coatings on aluminium, are considered. These films give excellent reflectance over a wide waveband and have high resistance to abrasion and corrosion. Other multiple-layer film combinations can be used as combined filters and mirrors. The reflectance curves of such mirrors having high infra-red and low visible reflectance are given. Finally, a method of producing epoxy-resin coated replicas is described. Silver, silicon monoxide and a thick aluminium film are evaporated on to the optical component in that order and then an epoxy-resin, preferably containing over 50% of finely divided silicon dioxide, is cast over the whole. The resin adheres to the thick aluminium film and the sandwich so formed may be separated at the silver layer which has poor adhesion to glass. After cleaning off the remaining silver film with nitric acid, a protected aluminium coated replica is left.

Article by G. Hass *J. Opt. Soc. Amer.* **45**, Nov. 1955 945-952

100/I

Improvements i.o.r.t. Coatings for Optical Elements

United Kingdom. A method is described of preparing high-refractive index optical interference layers of titanium nitride. The coatings are claimed to be at least as good as titanium-dioxide coatings as far as transparency, refractive index and durability are concerned and the optical absorption is low. The glass or other supporting surface is first coated with titanium by vacuum evaporation in the usual way. A tungsten boat carries the charge and evaporation is carried out at a pressure below 10^{-4} mm. Hg to give a uniform layer of the required thickness. The sample is then transferred to a small oven which is electrically heated to a temperature a little below the softening point of the glass base. The oven is filled with nitrogen for this operation and the gas supply pressure is held a little above atmospheric to prevent inward leakage of air. The nitriding process is continued for a period ranging from $\frac{1}{2}$ to 10 hours. The method provides a stable, durable, high-refractive index coating.

Kodak Limited W. J. Keenan, P. T. Scharf & W. F. Parsons *Brit. Pat. No.* 752,498

101/I

Multilayer Systems: Anti-Reflecting Systems, High-Reflecting Stacks and Interferences Filters

See Abstract No.: 43/III

102/I

Infra-Red Transmission of Synthetic Atmospheres I. Instrumentation

United States. Infra-red radiation is absorbed by various constituents of the atmosphere, chiefly by carbon dioxide, water vapour and ozone, and its knowledge of such absorption is valuable in a wide range of studies. Two approaches to the problem are possible to study the absorption spectra with high resolution instruments and ascribe to each absorption line its molecular cause, or to study bands rather than lines and relate the overall absorption with the bulk properties of the absorbent. The latter method was chosen for the present studies on carbon dioxide and water vapour under simulated atmospheric conditions. Nielson, Thornton and Dale have shown that:

$$\int_{\nu_1}^{\nu_2} A_\nu^- d\nu = \int A_\nu d\nu_1$$

where A_ν is the true absorption at frequency ν and A_ν^- is the observed absorption with an instrument incapable of infinite resolution. The integration is, in the first case, to be taken between the observed limits at which there is negligible absorption and, in the second case, over the entire width of the absorption band. This formula has been shown to be experimentally correct. Thus, wide slits and low resolution could be used to give a high signal-to-noise ratio and a simple frequency/absorption profile for planimetric integration. A 22 metre long absorption cell was used with a mirror system which passed the light through it up to 68 times, giving a total path length of slightly less than a mile, without the different light paths overlapping. The cell was vacuum-tight and could be held at less than 0.2 mm. Hg for several hours when isolated from the pump. A Dubrovin differential manometer was used for measuring pressures up to 2 cm. Hg and a mercury manometer and calibrated Bourdon gauge for higher pressures. Spectroscopically dry CO_2 could be admitted directly, or freshly boiled distilled water by evaporation, into the cell when the requisite pressure was obtained. 'Extra high purity' nitrogen was used with the CO_2 or water vapour as a non-absorbing gas for studies of pressure broadening. A Perkin-Elmer Model 90 thermostated double-pass manochromator was used to analyse the

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radiation. This, the infra-red source, and the focusing mirrors were enclosed in a box filled with spectroscopically pure dry nitrogen. The monochromator was calibrated using the spectra of pure gases and vapours. Its output was amplified with a Perkin-Elmer pre-amplifier followed by a Model 81 amplifier and was recorded on a Leeds and Northrop Model S chart recorder. The 13 cps rotating cylindrical radiation chopper in the monochromator being warmer than the rest of the instrument, gave a background infra-red spectrum that was determined and allowed for in all measurements. A table of sources, cell window materials, prisms and detectors used for the different wavelength bands is given. The results of the investigation, giving expressions for the total absorption under different conditions, will be the subject of subsequent papers.

Article by J. N. Howard, D. E. Burch & D. Williams *J. Opt. Soc. Amer.* 46, March 1956 186-190

Interferometry in the Infra-Red

103/I

United States. Operating under the condition of energy-limited resolution in the infra-red, the Fabry-Perot interferometer is shown to have a theoretical advantage by a factor of about 5 in resolving power over the diffraction grating. Tellurium films which have a high index of refraction in the infra-red are shown to absorb little energy from 5 to 20 microns. Multilayer films of tellurium and potassium bromide show high reflection and low absorption, appearing to be well suited for interferometer films. Tellurium is also shown to be suitable for filters for use in the region 5 to 25 microns.

(*Author*)

Article by R. G. Greenler *J. Opt. Soc. Amer.* 45, Oct. 1955 788-791

Vacuum Interferometer and Cadmium Oven

104/I

United States. The authors describe how they have constructed and used a Fabry-Perot interferometer in vacuum in order to overcome the effects of pressure and temperature changes. With a 5 mm. etalon one degree change in temperature at 3,000 Å will change the order number by 0.032 and 1 mm. Hg change in atmospheric pressure will change the order number by 0.256. These changes are of sufficient magnitude to be detrimental to wavelength measurements using long exposures. An interferometer is described in which the etalon is composed of plates 42 mm. in diameter and 10 mm. thick, of fused quartz, glass or natural quartz, separated by three Invar pins on a diameter of 35 mm. and mounted inside a housing which can be then placed inside a vacuum envelope. The thumb screws used for final adjustment of the parallelism of the plates have screwdriver slots into which fit screwdriver blades which can be adjusted *via* rotary vacuum seals from outside the vacuum envelope. The vacuum envelope is made from brass and has wrapped around it a soldered $\frac{1}{4}$ inch diameter copper tube through which can be circulated tap water or water from a constant temperature bath. The envelope is evacuated to a pressure of 10^{-2} mm. Hg or less by a good mechanical pump. The projection lens is sealed to the envelope using a gasket of amalgamated lead and held in place by a ring-retaining screw. Diagrams and a sectional view of the interferometer and housing are given. The authors further describe a Michelson-type lamp, constructed to international standard dimensions which is mounted inside a well-insulated box, the temperature of which can be held at 315°C, 260°C or 150°C by means of two heaters mounted inside the box running together, with one controlled by a thermostat and running continuously or with one only running controlled by a thermostat. The Michelson lamp has aluminium electrodes but higher melting point material is recommended as a precaution against inadvertently increasing the current through the tube thus melting the electrodes. The lamp contains the stable cadmium isotope 114, sealed off in 1 mm. Hg or argon. A diagram shows a typical experimental arrangement for comparing mercury-198, from a discharge tube excited by V.H.F., with cadmium-114. The pressure within the vacuum casing is measured using a thermocouple gauge (Westinghouse type 3T). A system using the vacuum interferometer and cadmium lamp can be used to measure the refractive indices of non-corrosive gases with a high degree of accuracy.

Article by K. B. Adams & K. Burns *J. Opt. Soc. Amer.* 46, Jan. 1956 36-38

Broad-Band Multilayer Film for Fabry-Perot Interferometers

105/I

United States. Multilayer dielectric films of high reflectance, widely used in interferometry, have until now been made with alternate equal optical thickness of high and low refractive index material. These have the disadvantage of a narrow band width, over which they have high reflectance. An upper limit is set to the number of layers used, with equal optical thicknesses, by the imperfections of the surfaces of available interferometer plates. Broad band-width cannot therefore, be obtained by indefinite increases in the number of layers. Penselin and Steudel have recently tried varying the thickness of the individual layers arbitrarily. This sometimes resulted in a significant broadening of the region of high reflectance without reducing that reflectance below the optimum of 0.95. The authors have produced a fifteen-layer film of zinc sulphide and cryolite with the layer thicknesses of differing magnitudes. The reflectance curves based on the selected combinations of layer thicknesses were calculated, using a matrix method, with a card-programmed computer. A considerable increase in reflectance range was produced, but irregularities in the region of high reflectance had to be smoothed out. The method of mathematically calculating the thickness adjustments to effect this is described. The reflectance of the films is compared, graphically, with that of conventional equithickness films.

Letter by P. W. Baumeister & J. M. Stone *J. Opt. Soc. Amer.* 46, March 1956 228-229

The Reflecting Multi-Dielectric Layers Applied to the Fabry-Perot Interferometer. Theoretical and Experimental Studies of the Layers

106/I

France. This article reports the final part of an investigation of the properties of multiple dielectric films of the type employed as semi-transparent mirrors in the Fabry-Perot Interferometer. The results of the investigation are discussed under 2 categories: (*a*) observations and conclusions with respect to the supposedly uniform thicknesses of the layers and (*b*) observations and conclusions with regard to absorption and diffusion caused by defects in the surfaces. Regarding (*a*), where the thicknesses vary by lambda/4 the loss in precision for a given

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wavelength is no longer negligible. This loss increases with the number of layers prepared. A method facilitating precision control of layer thickness is therefore imperative and details are given of a method for the purpose, evolved by the author. Regarding (*b*), absorption has an adverse effect on precision and transparency; it leads to an absorption quantity A_m which is independent of the number of layers used and of the thicknesses employed, as long as the latter are in the neighbourhood of lambda/4. Diffusion phenomena caused by irregularities in the surface play a more important part than intrinsic absorption, in particular in the case of zinc sulphide-cryolite combinations (in the middle of the visible spectrum). Diffusion will result in an apparent absorption which is not under control. It is an indispensable requirement therefore to overcome the diffusion effects in the layers. The Fabry-Perot calibration plate can be of considerable assistance in such studies. With the present means available multi-dielectric layers for the visible spectrum can be prepared having the following properties: Reflection–97%, transmission–2.25%, absorption–0.75% (transparency 50%), the absorption being due partly to external diffusion and partly to internal diffusion.

Article by P. Giacomo *Rev. Opt.* **35,** Aug.-Sept. 1956 442-467

107/I

Microscopical Measurements of Optical Path-Difference by Means of Coloured Birefringent Interferences and a New Compensation Method

Sweden. The apparatus described overcomes the disadvantages inherent in birefringent compensators when measuring optical path differences of light passing through small objects in a microscope. An isotropic system is achieved by using a rotatable glass wedge in conjunction with a Francon eyepiece. The thickness of the Savart plate in the latter is chosen so as to give a suitable sideways displacement between the two interfering wave-fronts somewhat larger than the enlarged image of the object detail to be measured. Different optical paths length in the two resulting images give rise to different interference colours. The glass wedge is rotated for colour correspondence of one of the images and the undistorted background as seen through a central hole in the wedge, which serves as a reference. The angle between this position of the wedge and that when colour correspondence is obtained with the second image enables the path difference to be calculated. Under ideal conditions an accuracy of about ± 10 Å in optical path difference can be obtained; this requires a regular object which provides relatively large and uniform detail for comparison. The method has been used for measuring the optical path difference of various objects:—thin films of evaporated zinc sulphide; silver bromide crystals in photographic emulsions; blood corpuscles. Examples of results obtained for path difference of different cell components in thin sections of pollen grains and spores measured in air and water respectively are given.

Article by L. P. Johansson & B. M. Afzelius *Nature* 178, 21.7.1956 137-139

108/I

Measurement of the Thickness of Thin Films by Multiple-Beam Interference

United Kingdom. Discrepancies have been found in measurements of film thicknesses by multiple beam interferometry methods. Avery reported thickness values for a silver film to be 25% greater when chromium was employed as the contouring overlayer instead of the more usual silver. This was not confirmed by Heavens who found no discrepancy. In the present experiments a silver film was evaporated on to a glass substrate and overlaid partly by chromium and partly by silver. All three evaporations took place without admission of air to the chamber, a mechanical device being used to position the substrate correctly in each case. The substrate was placed at 30 cm. from the chromium and silver source and the rates of evaporation were controlled at between 1 and 60 Å/sec. for the silver film and at 20 Å/sec. and 3 Å/sec. for the silver and chromium overlayers. Measurements of film thicknesses by multiple beam interferometry on the silver and chromium overlayers are given in tabular form. Discrepancies observed in these measurements disappeared when the chromium overlayer was coated in turn with an opaque silver film. It is concluded that the discrepancies in thickness measurements are caused by differences in the phase change that occur on reflection from the metal surface. The magnitude of the phase change is related to the film thickness and is only constant above a certain value of film thickness, *e.g.* 500 Å for silver. In the case of a thinner film, *i.e.* a non-opaque overlayer, a difference in the phase change occurs since the underlying substance is different. Further investigations are proceeding to determine the critical chromium thickness and the variation of phase change with the thickness.

Article by C. Weaver & P. Benjamin *Nature* 177, 2.6.1956 1030-1031

109/I

Measurement of Aluminium Film Thickness

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110/I

Optical Instruments for the Vacuum Ultra-Violet

United Kingdom. The operating pressures employed in optical instruments designed to work in the near vacuum ultra-violet (N.V.U.V.) ranging from 2,000 Å to 1,200 Å and in the far vacuum ultra-violet (F.V.U.V.) ranging from 1,200 Å to 200 Å are governed (*a*) by the nature of the optical materials used, (*b*) by the optical path length, (*c*) by the absorption properties of the residual gases and (*d*) by the nature of the work, simple wavelength measurements or intensity measurements. 30% absorption of the radiation by residual gases can be tolerated for the former whilst an absorption under 1% is required for the latter. Typical figures for a prism instrument of optical path 30 cm. operating in the N.V.U.V. are p (1%)–5×10^{-4} mm. Hg, p (30%)–1×10^{-2} mm. Hg. For a concave grating instrument with optical path 200 cm. in the F.V.U.V. the figures are p (1%)–10^{-4} mm. Hg, and p (30%)–3×10^{-3} mm. Hg. A static, clean, leak-free, vacuum system is essential for instruments measuring absorption and is preferable to continuous pumping for most spectroscopy. Great attention must be given to vacuum engineering details. Micro and macroscopic porosities must be avoided and welds and joints reduced to a minimum. O-ring seals are used at joints and where seals are necessary round rotatable shafts. Seals

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for translating motion generally employ an expanding bellows. Controls which it is desirable to operate from outside the vacuum system and therefore require to be fitted with some types of sealing device include (*1*) control of camera plate-holder, (*2*) control of shutter for exposure, (*3*) adjustment of focusing slit width, (*4*) movement of a mirror to check alignment, (*5*) a sliding valve to isolate the camera box for plate changing. In grating spectrographs and monchromators it is also desirable to have a single control for altering grating angle with a compensating translating motion for focusing purposes. The optical materials used in V.U.V. are selected for the qualities regarding transparency, dispersion, refractive index and reflection coefficients in the required range. The reflection coefficient of quartz, natural and synthetic, increases down to 1,200 Å, where it gives nearly 25%. Cellophane windows are usable for F.V.U.V. work down to 300 Å. Silicon monoxide and aluminium oxide films are also used.

Article by R. W. Ditchburn *Optica Acta* 3, June 1956 74-80

New Krypton Light Source for the Vacuum Ultra-Violet 111/I

See Abstract No.: 72/I

Band Spectra Emitted by Strontium and Barium in Arcs and Flames 112/I

United Kingdom. The author points out that visual observations on the band spectra of Sr, and Ba were made as long ago as 1823, but that the strongest flame bands have not been analysed, although it has been suggested that some of them are due to diatomic metal oxides. Recent suggestions that these flame bands might be due to hydroxide molecules led to experiments by one of the authors with Ca, in which arcs in air at atmospheric pressure and 'vacuum' arcs in H_2O and D_2O were studied. An isotope shift confirmed that bands were due to CaOH (or CaOD). It was also found that the bands obtained with the arc in air were slightly different from the flame bands, with a complex structure suggesting that they might be due to a polymer, *e.g.*, the dimer of the oxide. The present paper deals with comparable experiments with Sr and Ba. The assignment of these bands is important for the determination of dissociation energies and also in astrophysics. In the experiments, the arc in air was formed between 1 cm graphite poles, running at 220V d.c., 6-8 A, the salts being packed into a small hole in the graphite. The 'vacuum' arc was run between graphite electrodes in vapour of H_2O or D_2O at a few mm. Hg, with slow continuous pumping to sweep out hydrogen and other decomposition products. An oxy-hydrogen flame was also used, a commercial welding burner having the salt introduced by holding a rolled-up filter paper containing strong salt solution or crushed salt crystals. A special burner in which a spray of salt solution is carried into the flame by a stream of oxygen is briefly described. The spectroscopes used were a Hilger medium glass spectrograph, a 2-prism glass Littrow type (dispersion 6 Å per mm. in the orange) and (for the case of the Sr arc in air) a 21 ft. concave grating spectroscope (dispersion 1.23 Å per mm.) Plates sensitive to 8,500 Å were used. The plates reproduced show the Sr arc in air, in water vapour and in heavy-water vapour for the region 5,900–7,000 Å and similar spectra for Ba in the region 4,800–6,500 Å, together with higher dispersion plates for Sr in air covering 6,400–6,700 and 5,930–5,990 Å. There are also plates at the medium dispersion for Sr in the oxy-hydrogen flame, including the effect of changing the concentration of the solution sprayed into the special burner. The spectrum of Ba in this flame is shown at the low dispersion. In general, clearer bands were obtained with Sr than with Ba, but the isotopic shift observed supports the suggestion that the bands at 6,050, 6,460, 6,590, 6,675, and 6,820 Å should be assigned to SrOH (SrOD), while those obtained with Ba at 4,870, 5,120, 7,120–7,580 and 7,830–8,390 are similarly assigned to the hydroxide. With the Sr arc in air distinct bands were found at 5,950 and 6,050 Å, together with a considerable amount of band structure (different from that of the flame spectra) in the far red. The high-dispersion plate shows the very complicated structure of the 5,950 band, which is attributed to a polyatomic emitter. The bands in the red are considered too complicated for analysis, but a study of the effect of solution strength (using the special burner) on the 5,950 and 6,050 Å bands suggested that for the latter (due to SrOH when using a spray) the strength of the band is proportional to concentration, but for the former (not found in the water-vapour arc) the strength was proportional to a higher power than the first of the concentration. It is believed to be due to Sr_2O_2. In the case of Ba, the results did not allow any conclusion on this point. In the discussion, a table is given showing the comparison between hydroxide, complex oxide and fluoride bands for Ca, Sr and Ba. It is concluded that the existence of the hydroxide and complex oxide spectra greatly complicates the determination of dissociation energies for CaO, etc.

Article by M. Charton & A. G. Gaydon *Proc. Phys. Soc.* 69A July 1956 520-526

Spectral Emissivity of Rhenium 113/I

United States. The emissivity e_λ of a radiating surface is defined as

$$\varepsilon_\lambda = \frac{N_\lambda}{N_{o\lambda}}$$

where N_λ is the spectral radiance of the surface measured in a direction normal to the surface at a given temperature, and $N_{o\lambda}$ is the corresponding spectral radiance of a black body at the same temperature. The measurements reported here were made for wavelengths between 0.35 μ and 2.8 μ, and at temperatures between 1,537° and 2,772°C. The results obtained at $\lambda = 0.65$ μ are compared with results published by other workers. A hollow rhenium tube with a 0.020 inch diameter hole in the side to give black body radiation was mounted in a vacuum bulb with a quartz window. The tube was heated electrically and an optical system was used to focus the image of the hole so that hole radiation passed into a monochromator. For the initial measurements at temperatures below 2,200°C the bulb was evacuated to 10^{-6} mm. Hg and baked at 400°C for an hour. After cooling, the rhenium was heated to 2,300°C and pumping continued until a pressure of 5×10^{-6} mm. Hg was reached, when the tube was sealed off from the vacuum system. Before making measurements at temperatures

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Article by D. T. F. Marple *J. Opt. Soc. Amer.* 46, July 1956 490-494	above 2,200°C the bulb was re-connected to the vacuum system, baked at 400° and the rhenium tube operated at 2,200° for fifteen minutes. When cool the bulb was filled to 50 cm. pressure with argon, and sealed off. The monochromator slits and the detector output were adjusted for full-scale deflection of the output meter and the optical system was then adjusted so that radiation from one of the free surface areas adjacent to the aperture passed to the monochromator. The fraction of full-scale deflection produced by this radiation is the emissivity. The emissivity, determined in the present experiments, at $\lambda=0.65$ μ agrees well with previous measurements in the range below 2,200°C but disagrees slightly at temperatures above that value. The author concludes the article with a discussion comparing his experimental results with the predictions of the Hagen-Rubens relation.
114/I	**A Furnace for Obtaining Optical Spectra of Radioactive Elements** See Abstract No.: 225/I
115/I	**Application of Radioactive Materials to the Problem of Metals of Very High Purity** See Abstract No.: 224/I
116/I	**Handling Alpha-Active, Pyrophoric Materials II. Glovebox Design and Construction** See Abstract No.: 104/II
117/I Article by A. H. Turnbull *Vacuum* 5, Oct. 1955 131-156	**Applications of Vacuum Technique in Atomic Energy Research** *United Kingdom.* The purpose for which vacuum equipment and techniques are used at the Atomic Energy Research Establishment, Harwell, are described. Reference is made to metallurgical applications, measurement of the gas content of metals, the production of thin films, vacuum technique in mass spectrometry, and high power r.f. valve manufacture. The vacuum systems of the proton linear accelerator and the Mark II heavy element electromagnetic separator are described and an account is given of some of the research work, past and present, of the Vacuum Group.
118/I	**Space-Charge and Ionisation Phenomena in Constant-Gradient Proton Synchrotron** See Abstract No.: 50/IV
119/I Article by J. Seiden *J. Phys. Radium* 16, Dec. 1955 917-925	**The Diffusion of Protons Through the Residual Gas in a Synchrotron I. Elastic Scattering** *France.* The accelerated protons in a synchroton undergo during their passage in the vacuum chamber many collisions with the molecules of the residual gas. Such collisions may cause considerable proton losses. The multiple elastic scattering sets up oscillations the amplitude of which is calculated from Moliere's law. This amplitude is proportional to the square root of the gas pressure in the vacuum chamber and inversely proportional to the square root of the energy of injection and the energy gain per revolution. The theory is applied to various synchrotrons under construction. When applied to the strongly converging synchrotrons of M.I.T. the theory shows that the amplitudes produced by multiple scattering are greater than half the vertical height of the vacuum chamber. The proton losses through single elastic scattering are calculated and are found to be proportional to the gas pressure and inversely proportional to the energy of injection and the energy gain per revolution. 6% of the protons are lost through single scattering in the Brookhaven cosmotron and 14% would be lost in the M.I.T. synchrotron.
120/I	**Multiple Target Nuclear Magnetic Resonance Cryostat** See Abstract No.: 119/II
121/I	**An Improved Helium Liquefier and Cryostat** See Abstract No.: 118/II
122/I	**The Physics of Extreme Conditions II. Matter at Low Temperatures** *United Kingdom.* Temperatures have been achieved in the laboratory which are far lower than anything observed in nature. The writer gives a simple description of the thermodynamics of producing low temperatures. The importance of the production of liquid gases is emphasised and helium liquefiers operating on the Claude principle, such as the Kapitza and Collins liquefiers, and the Linde principle, used at the Kammerlingh Onnes

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and Clarendon Laboratories, are described. The author continues with a discussion of the importance of low-temperature work to Physics generally and then concentrates on two specific low temperature effects:— Superconductivity and the phenomena associated with liquid helium II. Some metals when cooled below a certain characteristic temperature, lose all electrical resistance. This effect was discovered by Kammerlingh Onnes in 1911 and is known as superconductivity. As an illustration of this effect, a photograph is shown of a lead sphere supported in mid-air by the magnetic forces due to persistent currents in two superconducting lead rings positioned beneath it. This lack of resistance has been used in devices for measuring very small electrical voltages or fluxes of thermal radiation. Only recently has any attempt to explain the phenomena proved successful. Helium is remarkable in existing as a liquid at absolute zero, and therefore being capable of being perfectly ordered in some way in the liquid state. Secondly, liquid helium is remarkable, because it completely changes its behaviour at 2.19°K. Its viscosity disappears entirely and the property of forming layers of about 100 atoms thick on all surfaces, irrespective of their inclination, appears. The term 'superfluidity' is used to describe these effects and the liquid exhibiting them is known as liquid helium II. Temperatures below 1°K and down to 0.001°K can be achieved by adiabatic demagnetisation of a precooled paramagnetic salt. The elementary electronic magnets are aligned in a magnetic field to lower the disorder of the system, the heat generated by this is removed and subsequent removal of the applied field results in a cooling of the salt. One demagnetisation can lower the temperature from 1°K to 0.01°K and two, to 0.001°K. At these temperatures, mainly, studies of magnetic fine structure are undertaken.

Article by G. O. Jones *Discovery* **16**, Nov. 1955 471-477

Total Emissivities and Absorptivities of Some Commercial Surfaces at Room and Liquid-Nitrogen Temperatures 123/I

United States. Experiments have been conducted to measure heat transfer by thermal radiation between two concentric spherical surfaces, the outer at room temperature, i.e. 300°C and the inner at liquid nitrogen temperature, 77.3°K. A 25-litre commercial liquid nitrogen Dewar was disassembled and the outer shell made demountable at a point near the upper end of the neck and at the equatorial joint. A pumping aperture was provided and, at the bottom, a second aperture to connect with a pair of ionisation gauges. To avoid these apertures (and that round the neck) acting as black body radiators, radiation shields were provided over each. The evaporated nitrogen gas was collected and the rate of evaporation calibrated in terms of heat intake by means of an immersed heater (a 5.6 ohm resistor) supplied from a d.c. source. It was established, both by calculation (ignoring reduction due to cooling by evolved gas) and by heat input experiments that the conduction down the supporting neck was less than 3% of other heat transfer mechanisms. Experiments also showed no effect due to liquid level in the inner sphere. 10 copper-constantan thermocouples were used to monitor the outer shell temperature. In order to avoid condensation of volatile substances on the cold surface, care was taken to use a clean system and a cold trap was included above the diffusion pump to eliminate backstreaming of oil vapour. A series of readings taken of heat transfer *vs.* interspace pressure, P_c, with the outer shell at 299°K, gave the heat transfer q_c due to gas conduction alone as $q_c = 2.17 \times 10^4 P_c$ watts (P_c in mm. Hg). During most of the tests P_c was less than 3×10^{-6} mm. Hg. The surfaces used were silver-lume, 'matte' silver, dry buffed silver, matte gold, gold wash, dry buffed gold, polished gold, polished copper, stainless steel spinning rubbed with fine emery cloth and a black body surface produced by covering the inner shell with drafting tape so as to provide a basis for calculation of the emissivity factor, F_E. The radiation heat transfer, $q_R = \sigma A_i F_E (T_o^4 - T_i^4)$ where A is the surface area of inner sphere, σ is the Stefan-Boltzmann constant, T_o an T_i temperatures of outer and inner spheres respectively. F_E is the direct ratio of heat transferred by radiation alone for the surfaces used to that if both surfaces were black bodies. The silver-lume plating process was done by the Hanson-van-Winkle-Munning bath (a KCN plating bath with organic additions to reduce grain size) which under ideal conditions of current density, composition and agitation may produce a brilliant deposit. No buffing was used in this case. The matte surfaces were unbuffed electroplated surfaces dull or milky in appearance. The absorptivities $\alpha_{i,o}$ and emissivities ε_o were derived from the emissivity factors F_E, using the specular reflection equation (in which the area ratio does not occur).

$$F_E = \frac{1}{(1/\alpha_{i,o}) + (1/\varepsilon_o) - 1}$$

The conclusion drawn is that, if electroplated gold or silver surfaces are used, they should not be buffed, and the silver-lume surface is the most preferable. However good a radiation surface may be, dirt or condensed vapour will ruin its effectiveness. It is computed that the absorptivities, are accurate to $\pm 10\%$ and the room temperature emissivities to $\pm 20\%$ but that the two errors are not likely to be additive. The emissivities and absorptivities of the surfaces tested during the work reported here are given in a table, reproduced below.

Material	$\alpha_{i,o}$*	ε_o†
Silver-lume	0.0083	0.017
Matte silver	0.012	0.020
Dry buffed silver	0.016	
Matte gold	0.014	
Gold wash	0.015	
Dry buffed gold	0.016	
Polished gold (kerosine buff)	0.018	0.0225
Polished copper (solid sheet)	0.015	0.020

*Absorptivity for a surface at 77.3° K for radiation from a 300° K surface.
†Emissivity for a 300° K surface.

Article by F. J. Zimmermann *J. Appl. Phys.* **26**, Dec. 1955 1483-1488

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124/I

On the Dynamic Temperature Response of a Vacuum Calorimeter

United States. Refers to experiments (to be published elsewhere) to measure the specific heat of magnetite at liquid He temperatures in which the time constants of the heating and cooling curves were less than one minute so that lags due to galvanometer response and to the thermal conductivity of the specimen had to be considered. Existing methods of obtaining the s.h. from the heating and cooling curves became uncertain. The graphical method of Keesom and Kok, for instance, is briefly described—both heating and cooling curves are assumed to be exponential and a simple construction gives the 'corrected' temperature rise. This will fail in the presence of time lags, as the curves will not be exponential, and the corrected curve shapes calculated by Vasileff are shown. The effect of finite thermal conductivity of the specimen is shown to be greatest near the beginning and end of the heating period and the more serious, the shorter the heating period. A method is then developed for the case of a semi-infinite cylinder, in which the excess temperature is taken at 3 points on the cooling curve and a function obtained equal to the ratio s.h./rate of heating. It is concluded that the effect of the finite conductivity of the cylindrical calorimeter is least if the thermometer is located on the axis of the cylinder. The effect of the lag in the galvanometer response is then examined, assuming a linear relation between the excess temperature and the deflecting voltage. An expression is obtained for the deflection as a function of time which involves the time constants of both the calorimeter system and the galvanometer; the maximum deflection occurs after the end of the heating period and it is shown that the new method of treating the cooling curve should be applied after the maximum deflection has been reached. An example is given of a computation by this method in which heating was carried on for some 13 sec. at 4 μW; the time constant of the calorimeter was 33.7 sec. and the time constant for the lags about 1 sec. The error in the computed value of heat capacity is estimated as less than 6%; a correction could be made from the ratio of time constants.

Article by J. S. Kouvel *J. Appl. Phys.* 27, June 1956 639-642

125/I

Article by D. W. Plester S. E. Rogers & A. R. Ubbelohde *J. Sci. Instrum.* 33, June 1956 211-212

Calorimetry by the Method of Mixtures

United Kingdom. A vacuum calorimeter is described, suitable for measuring heat contents of condensed phases at high temperatures. The heat of fusion of potassium thiocyanate has been evaluated as H_f–3.39 $\pm$ 0.05 kcal/mol. (mean deviation).

(*Authors*)

126/I

Estimating Steam Film Coefficients Under Vacuum

See Abstract No.: 133/III

127/I

Sublimation Figures in Nickel, Copper and Zinc

See Abstract No.: 221/I

128/I

Properties of Evaporated Metal Films Related to Their Use for Surface Temperature Measurements

See Abstract No.: 116/II

129/I

Improvements i.o.r.t. Deposition of Films and Coatings

United Kingdom. A novel method of producing a contoured surface by vacuum evaporation is described. The method can be employed to produce a facetted surface mirror for use in an interferometer, for instance. In a typical arrangement the metal is evaporated from a source (surface area $\frac{3}{8} \times \frac{1}{2}$ inch) at the base of a vacuum chamber through a stop, positioned 1 inch above it, with a rectangular slit $\frac{1}{10} \times \frac{3}{8}$ inch in dimensions. Above this is a grid formed by parallel wires (0.006 inch diameter), spaced 0.006 inch apart, 0.178 inch away from the substrate which, in turn, is 3 inch. from the stop. During evaporation, the grid causes a combination of umbrae and penumbrae on the substrate resulting in a variation of the thickness of the deposit, a maximum being reached at the point mid-way between 2 wires, every time. By altering the spacings and dimensions, flat plateaux or valleys may be formed, and by employing a cross grid the effect can be produced in two directions.

J. St. L. Philpot, D. E. Andrew T. A. J. Jaques & National Research Development Corp. *Brit. Pat.* 712,105

130/I

Improvements i.o.r.t. Apparatus for Forming Coatings by Evaporation and Condensation of the Coating Material

See Abstract No.: 26/III

131/I

The Effect of Incident Atomic Velocity on the Structure of Evaporated Silver Films

Canada. The work reported here was carried out to determine the effect of incident particle velocity on the structure of thin silver films evaporated and condensed on to glass in vacuum. Controversy exists in the literature on this point. Silver was used in this series of experiments because of its markedly grainy structure. Observations on granulating were made directly by transmission electron micrography and indirectly by measurement of the film resistivity. Two methods of reducing the velocity of silver atoms incident on to a flat microslide were used:— (*i*) Diffusion through nitrogen gas at a pressure of 3 μ Hg, (*ii*) reflection from a

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suitable surface. Conventional vacuum techniques were employed: The silver was evaporated from a shielded tungsten foil source and the microslides were given ionic bombardment in a glow discharge as a final cleaning process. The apparatus was capable of evacuation to 10^{-2} μ Hg. Deposition was carried out slowly over a period of 100 secs. with a very low beam intensity. The film thickness was measured by multiple beam interferometry. From the work of Cravath it can be shown that the average energy of silver molecules passing through nitrogen can be reduced to the mean nitrogen molecule velocity in six or seven collisons. To ensure this condition in the diffusion experiments, it was calculated that a nitrogen pressure of 3 μ Hg was necessary. In order to give a range of thicknesses during each evaporation, the slide was set at 45° to the incident beam. Thick silver electrodes were provided for resistance measurement, and the electron microscope mounts were put along the edges of the slide. The silver films were aged in vacuum and in air before resistivity was measured. In the reflection experiments, certain tests were made to find the most suitable reflecting surface. 'Teflon' was finally chosen, because of its stability in a glow discharge. The slide and microscope mount were placed in such a position that silver atoms could be received only by reflection or scattering from the 'Teflon'. The results of both series of experiments were compared with direct silver evaporation under the same conditions. A graph shows the logarithm of resistivity plotted against thickness. There is very little difference of resistivity with method in films above 200 Å thick. Films deposited at 3 μ of Hg become conducting at about 110 Å. Films deposited by reflection become conducting at about 135–140 Å and directly deposited films at 160 Å. These results are confirmed by electron micrographs which show that in films of the thickness referred to, the grains are just beginning to join. In the following discussion, the authors give a qualitative explanation of their results. Films formed from higher energy particles will have more mobility to move into preferred states and will therefore exhibit coarser structures. The directly evaporated silver in these experiments had an incident energy of about 1,300°K, whilst in the 'diffusion' experiments the energy had been reduced to about 320°K. The 'reflected' particles should have had an energy intermediate between the above. Correspondingly, it was found for a given film thickness: Directly evaporated silver had a very aggregated structure compared with the diffused silver, the structure of reflected films being intermediate.

Article by R. A. Aziz & G. D. Scott *Canad. J. Phys.* **34**, Aug. 1956 731-736

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Effect of Magnetic Field Strength During Condensation on the Coercivity and Form of Vapour-Deposited Iron 132/I

United States. Vapour-deposited iron films depend for their particle size and shape, and their coercivity characteristics on the temperature and magnetic field strength during deposition. A vacuum evaporation apparatus was specially designed to investigate this relationship. It consisted of a fused quartz chamber (diameter 2 inch., length 12 inch.) with an alundum crucible (evaporation area-8 cm^2) loaded with 40 g. of magnetic-grade ingot iron. This was induction-heated to 1,600–1,650°C and gave an evaporation rate of 4–8 g/hr-cm^2. The pressure maintained by the vacuum system was 5×10^{-6} mm. Hg at the chamber base 0.1–0.2 mm. Hg at the melt surface and 10^{-4}–10^{-3} mm. Hg at the substrate surface. The copper substrate formed part of the wall of a condenser which contained liquid nitrogen, a dry-ice alcohol mixture or boiling water, dependent on the temperature being investigated. The magnetic field was applied normally to the substrate surface. Ten-minute evaporation periods were used to deposit 0.2 g. of iron. The deposits were examined microscopically. Coercivity measurements correct to ± 5 oersteds were made using Meikeljohn's method. Coercivity results for −196°C, −78°C and +10°C are given in a graph. The particles in the +10°C deposits were highly asymetrical and about 100 μ in length while the lower-temperature deposits with highest coercivities were equiaxial in shape with diameter 10–20 μ. Line broadening was observed in the diffraction patterns of the vapour-deposited iron and was attributed to strains. The observed coercivities were within the limits prescribed by the strain theory.

Article by A. J. Griest, J. F. Libsch & G. P. Conard *J. Appl. Phys.* **27**, Sept. 1956 1022-1024

An X-Ray Study in High Vacuum of the Structure of Evaporated Copper Films 133/I

United Kingdom. This investigation was undertaken in order to measure the sizes of the constituent crystallites in evaporated copper films, both at liquid oxygen and at room temperature. A vacuum x-ray powder camera was constructed which enabled the copper film to be deposited *in vacuo* on a glass substrate cooled to liquid-air temperature and to be maintained free from gaseous contamination for many hours while x-ray diffraction patterns were photographed. The camera was designed to record a number of Debye-Scherrer diffraction lines in a form suitable for examining line profiles and particle size broadening. During the annealing process to which the copper films were subjected the particle size may change by an order of magnitude. In order to obtain adequate sensitivity it was necessary to study more than one diffraction line, observing a line at a small value of θ (The Bragg angle) before and one at a larger value of θ after annealing. The (200) and (311) copper lines (θ=22.5° and 45° respectively with Cu Kα radiation) were chosen. In order that a reasonable diffracted x-ray intensity could be obtained from copper films only 2,000 Å thick without using a wide entrance slit, a focusing camera of the Seeman-Bohlin type was constructed. Details of the camera are given together with the methods used for setting it up and depositing the copper film on the glass substrate. Provision was also made for exposing the film to oxygen when required. It was found that the film consisted of aggregates of randomly-oriented crystallites of nominal size 40 Å, this dimension being reproducible and almost independent of the nature of the substrate when deposited at −183°C. When the films were annealed at room temperature in a vacuum which precluded the chemisorption of oxygen or other reactive gas, there was a large, rapid and irreversible increase in the nominal particle size to at least 400 Å. The chemisorption of a saturated monolayer of oxygen at −183°C before the annealing took place almost prevented this re-crystallisation and the particles grew to only 60 Å. The chemisorption of a smaller quantity of oxygen, sufficient to give only a fraction of a monolayer, inhibited the annealing process but, although it could prolong it for several days, it did not prevent the film from re-crystallising to the same extent as in the absence of oxygen. The results are in qualitative agreement with resistivity and gas adsorption data for copper films. The results indicate that surface diffusion plays a leading part in the re-crystallisation of the disordered films.

Article by H. D. Keith *Proc. Phys. Soc.* **69B**, Feb. 1956 180-192

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134/I

Stress Annealing in Copper Films

United States. The measurement of the intrinsic tensile stress in copper films deposited on a mica substrate *in vacuo* at various temperatures below room temperatures is described. The mica is clamped at the edges by a set of copper blocks; these facilitate the removal of heat during deposition. In order to measure the stress, the clamping blocks are removed, without breaking the vacuum, except at one end of the substrate which now forms a cantilever beam which tends to curve because of the stress in the film. A force is then applied to the free end of the beam by the needle of an electrical meter movement to balance the force due to the stress. Measurements on films of thicknesses between 900 Å and 1,500 Å deposited at substrate temperatures between −150°C and +75°C and followed by annealing at various temperatures show that the stress is reduced as annealing is carried out at progressively higher temperatures up to +75°C, but that the stress increases again for higher annealing temperatures. The most rapid change takes place at temperatures near +25°C.

Letter by R. W. Hoffman & H. S. Story *J. Appl. Phys.* **27**, Feb. 1956 193

135/I

Spirals Developed on Single Crystals of Copper by Heating to High Temperatures in High Vacuums

United States. The appearance of spirals with steps of the order of 1 micron high is reported, easily seen at ×333 magnification, on single crystals of copper after evaporation has taken place at temperatures near melting point. The steps were usually round the (111) pole and were observed on OFHC copper of both 99.96% and 99.999% purity. In one series of experiments, a sphere $\frac{5}{8}$ inch in diameter was turned at the end of a single-crystal rod and prepared by etching and polishing. It appeared smooth at ×1,000. It was then suspended in a 200 ml. Pyrex bulb, annealed in H_2 for 1 hr. at 500°C and vacuum-baked for 16 hr., at the end of which treatment the pressure was 2×10^{-9} mm. Hg. Metal was then evaporated by induction-heating to 1,050°C at about 5×10^{-9} mm. Hg. The spirals and pits were then observed. Similar results were obtained when a crystal was grown with an hemispherical end to avoid machining. It was, however, found possible to avoid the formation of spirals by careful control of the conditions of crystal growth in some cases.

Letter by F. W. Young Jr. *J. Appl. Phys.* **27**, May 1956 554

136/I

The Evaporation of Impurities from Silicon

United Kingdom. Silicon crystals can be grown by 'pulling' a solid crystal slowly from a liquid melt of silicon, the process taking place in vacuum. Impurities present in the melt may become concentrated there or enter the crystal, the latter process being inhibited by the tendency for impurites to be left in the liquid phase during crystallisation. The concentration of impurities in the crystal is therefore governed by their rate of evaporation and by the growth conditions. A theoretical analysis shows that the evaporation rate depends upon the molecular weight, the concentration, the partial molal heats of solution and the molal free energy of evaporation of the substances involved, as well as on physical conditions such as the area of evaporation. The impurities Ga, In, As and Sb evaporate rapidly, P, Al and Mn evaporate slowly while B, Fe and Cu evaporate extremely slowly from molten silicon. Consideration of the joint effects of evaporation and segregation of impurity leads to a determination of the critical growth rate that will produce a uniform distribution of impurity within the crystal. The table indicates the time of growth at a constant rate which produces uniform impurity when 100g. of silicon having the stated additive are grown into a crystal from a crucible having an area of 30 cm². The critical rate is independent of the quantity of the added impurity. The results of experiments on the addition

Impurity	P	As	Sb	B	Al	Ga	In	Cu	Fe	Mn
Time	3h	3m	0.5m	10h	5h	0.5h	5m	10h	20h	2h

of phosphorus to silicon support the theoretical analysis given. Boron, the only impurity from groups 3 and 5 which will not evaporate from molten silicon in vacuum in a reasonable time, is found to give crystals which are invariably of the *p*-type and, in certain cases, have a resistivity greater than 100 ohm cm. The effect of repeated addition of antimony, which is a fast evaporating substance, during the growth of a silicon crystal from a melt containing phosphorus is to produce a series of practically identical *p-n* junctions in the crystal. The distribution of impurity can be controlled by selecting (*1*) the chemical nature of the impurity (*2*) the growth rates employed and (*3*) the nature of the ambient atmosphere used when growing a crystal containing the junctions. Argon, present at a pressure of a few millimetres Hg, has a pronounced effect on the rate of evaporation.

Article by S. E. Bradshaw & A. I. Mlavsky *J. Electronics* **2**, Sept. 1956 134-144

137/I

An Improved Method for the Production of Single Crystals of Semiconductor Materials

Germany. An improved method is described for the production of single crystals of semiconductor materials such as germanium of silicon having a predetermined concentration of impurity centres. In previous methods where a seed crystal is gradually withdrawn from a melt originally prepared from the basic material in its purest form and then diluted with the desired impurity substance to the appropriate extent, it has been found that the concentration of impurity centres in the crystal does not remain constant over the full length of the crystal. The concentration tends to increase in the layers drawn from the molten mass at a later stage of the process. The present invention proposes to overcome this difficulty by adding to the mass further material during the drawing of the crystal, the additional material having a definite concentration of impurity centres and being introduced at such a rate as to keep the volume of the molten mass unchanged during the drawing of the crystal. In some cases, the added material must have the same concentration of impurity centres as that required in the

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crystal but if the ratio of concentration of impurity centres in the crystal to that in the molten mass is to be small and if the volume of the drawn crystal is not too great, the added material may have a concentration of impurity centres which is less than the desired concentration in the crystal. For example, if it is desired to draw *p* or *n*-conductive germanium single crystals with indium or antimony as the impurity substance, the added material can be germanium of a high degree of purity.

Telefunken G.m.b.H. *Brit. Pat.* 755,422

Useful Impurities in Semiconductors and Phosphors

See Abstract No.: 68/I

138/I

Grainless Phosphor Screens for T.V. Tubes and a Light Amplifier

See Abstract No.: 69/I

139/I

Spectral Energy Distribution Curves of ZnS: Ag and ZnCdS: Ag after Thermal Vacuum Treatment

See Abstract No.: 70/I

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Friction Phenomena in Vacuum

141/I
Article by O. Heilingbrunner *Vakuum-Tech.* 4, Jan. 1956 133-139

Germany. An experimental arrangement and procedure is described which permits assessment of the proportion of elastic collisions between molecules and the wall of a vessel. The results of the measurements are discussed and their significance with regard to the mechanism of friction in vacuum is investigated.

Apparatus for Friction Studies at High Vacuum

142/I

United States. A friction test apparatus employing coupled magnets is described, which permits friction studies of dry lubricants under high vacuum by measurement of the lag angle between the magnets. The test track of the apparatus is a stainless steel plate, which, with a glass cylinder and an O-ring seal, forms the vacuum chamber. On the plate rides a specimen holder, supported at its periphery by three pellets of compressed lubricant powder. The driven and driving magnets, made identically of Alnico V, are situated above and below the friction system, respectively. The driven magnet is supported by ball-bearings on an $\frac{1}{8}$ inch pivot shaft threaded into the plate, and is coupled for angular motion to the specimen holder. Octoil is used as lubricant. The driving magnet is below the plate, and is coupled to a variable-speed motor. This system is mechanically separate from the vacuum chamber. In operation, the position of the driven magnet is optically fixed by observation through a fixed telescope under stroboscopic illumination. The strobe-light is triggered by a pair of contacts, one attached to a rotatable angular scale and the other to the driving magnet shaft. The former is adjusted until the driven magnet is observed in the reference position, when the latter contact gives the position of the driving magnet. The lag angle between the two magnets is measured with and without the sample in position. By subtraction of the no-load angle (ca. 0.5°) from the load angle (not less than 5°), a measure of the coefficient of friction is obtained. Calibration of the system is possible by a knowledge of the torque for a given angle, weight of specimen holder, and diameter of track. Torque calibration may be made by an oscillation method, or directly with weights and pulleys. Agreement is good at small lag angles. Errors due to eddy currents or air damping may be ignored. Motor speeds equivalent to 0–60σ cm./sec. may be used. The no-load lag angle is independent of speed. Studies at various temperatures are made by use of an element and thermocouple embedded in the stainless steel plate.

Article by V. R. Johnson, G. W. Vaughn & M. T. Lavik *Rev. Sci. Instrum.* 27, Aug. 1956 611-613

Vapour Lubrication of Graphite Sliding Contacts

143/I

United States. It has previously been shown that the lubrication of graphite in a normal atmosphere is dependent on water vapour in the air at a partial pressure of several millimeters of mercury; in a vacuum, the graphite was found to wear away rapidly. The present paper describes investigations of the lubricating efficiency of straight-chain hydrocarbons and the corresponding alcohols and halides over a range of pressures. The apparatus consisted of an evacuated bell-jar containing the sliding contact mechanism which consisted of a copper slip-ring driven by an external synchronous motor through a magnetic coupling and two graphite rods bearing on it. Special precautions were taken to ensure that only single vapours of high purity were present during each experiment. The vapour pressure was measured by a Pirani gauge and was controlled by an external temperature bath. Graphs of the wear rate against pressure were of a similar shape for all the vapours tested, with a hysteresis effect observed in some cases as the pressure was raised and lowered. The pressure at which the curve approached zero wear rate was taken as the minimum lubricating pressure p_1, for that vapour. It varied from 0.00027 mm. Hg for 1-bromo-pentane to 3 mm. Hg for water. The ratio p_1/p_0, where p_0 is the saturation vapour pressure at the temperature of the apparatus, is then defined as the minimum relative 'humidity' required to lubricate graphite rods. It is found that p_1/p_0 decreases logarithmically with linear increase in the chain length of the molecules in the region 5 to 10 Å. In this region the required vapour pressure is equivalent to only a few parts per million in ordinary air.

Article by R. H. Savage & D. L. Schaefer *J. Appl. Phys.* 27, Feb. 1956 136-138

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144/I

Vapour Lubrication of Titanium and Zirconium

United Kingdom. The coefficient of friction is high ($\mu=0.5$ under most ordinary conditions) between Ti surfaces and boundary lubrication is difficult because the surfaces are covered by a thin oxide layer. If the surfaces are cleaned by heating *in vacuo* (10^{-3} to 10^{-4} mm. Hg) until some of the surface metal has evaporated, the friction is even higher, $\mu=1.5$ having been measured at room temperature, and rises higher still at temperatures above 300°C. Such conditions may be met in high-speed turning, so that lubrication is of practical importance. Admitting various gases and vapours to the vacuum tank (O_2, H_2O, certain fatty acids) was found to make little difference to the friction in contrast to the behaviour of copper surfaces. It has, however, been reported that a lamellar coating of molybdenum disulphide gives good lubrication between Mo surfaces in air, even at 300-400°C, and the dihalides of Ti have a similar structure to MoS_2. Experiments were therefore conducted in which the cleaned Ti surfaces (still *in vacuo*) were exposed to the vapour of iodine crystals. An immediate drop in friction was observed, from $\mu=1.5$ to $\mu=0.3$, and there was no appreciable increase with temperature up to about 400°C, above which the titanium di-iodide decomposes into the volatile tetra-iodide which evaporates. Very similar results are reported for Zr and for the effect of H_2S on Mo surfaces.

Note by G. W. Rowe *Brit. J. Appl. Phys.* 7, April 1956 152-153

145/I

Technical Aspects of Levitation

Holland. For the purposes of this report levitation of a body is defined as a state of either stable or indifferent equilibrium with respect to the earth in which material contact between the body and its environment is not essential. The possibilities and limitations of levitation by auxiliary gravitational forces, by reaction forces and by forces in electromagnetic fields are investigated. The provision of auxiliary gravitational forces requires an auxiliary body of so large a mass that it is impracticable for experimental purposes. The use of reaction forces of the type employed in rockets, for instance, has limitations indicated in basic considerations given in the report. Levitation by radiation pressure is not feasible and levitation by forces in electrostatic fields is theoretically impossible. Some success has been achieved in arrangements using forces in magnetostatic, stationary and quasi-stationary electromagnetic fields acting on diamagnetic or superconducting bodies *in vacuo*. Discussing practical applications, the author refers to ultracentrifuges and levitation melting.

Report by A. H. Boerdijk *Philips Res. Rep.* 11, 1956 45-56

146/I

High-Speed Rotating Cylinder for Rarefied Gas Dynamics Research

See Abstract No.: 18/I

147/I

Flow of Gases Through a Packed Bed of Silica Powder at Low Pressures

See Abstract No.: 18/IV

148/I

A Method of Determining Particle Size of Powders

See Abstract No.: 158/III

16 — CHEMISTRY — 16

149/I

Survey of Separation Processes—Other than Solvent Recovery

United States. The article deals with fission product separation processes for fuel recovery in nuclear reactor operation. The following four processes are considered: (*1*) Precipitation processes; (*2*) ion-exchange processes; (*3*) fractional distillation processes and (*4*) pyro-metallurgical processes. The latter have developed along two lines. One of these is concerned with reactor-blanket processing, and the other with reactor-core processing. Three types of operations have received the most attention for blanket processing to concentrate plutonium:— (*i*) Vacuum distillation. Plutonium can be concentrated by vacuum distillation from molten uranium at 1,500–1,800°C. More than 99% removal has been effected and experimental results agree with theoretical calculations. A table, reproduced below, gives the results of two typical runs. Work remains to be done on the design and

Vacuum Volatilisation of Plutonium from Molten Uranium

Temperautre °C	*Area* sq.cm./g.	*Time* min.	*Volatised* %
1,680	0.7	40	91
1,680	0.4	140	99

construction of the plutonium collectors. (*ii*) Salt extraction. Plutonium has been successfully recovered from uranium as the fluoride or chloride, which can then be reduced to metal. By repeating the extraction it should

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be possible to obtain all the plutonium in this way. (*iii*) Molten metals as extractants. Silver and magnesium are immiscible with molten uranium but have favourable capacities for plutonium extraction. The fraction of plutonium extracted by magnesium is independent of the concentration over a wide range but account must be taken of the high vapour pressure of magnesium at high temperatures. Using silver, the subsequent separation of plutonium is difficult, the preferred method at present is distillation of the silver. Neither of these methods is selective so far as separation of uranium and plutonium from other fission products (Cs, Sr, Ce, etc.) is concerned. Some work has also been done on a continuous re-crystallisation or zone-melting process but results are not encouraging, largely because of the extremely slow processing rates.

Article by S. Lawroski *Chem. Engng. Progr.* 51, Oct. 1955 461-466

Separation of Mixtures by Low-Pressure Rectification 150/I

See Abstract No.: 136/III

Trends in Fatty Acid Distillation 151/I

United States. The production of fatty acids by the hydrolysis of fats is exemplified in the manufacture of stearic acid and oleic acid, and the conditions of hot and cold pressings are discussed. Although these operations can produce good results from undistilled fatty acids, distillation eliminates certain disadvantages, such as tendency to decomposition and odour. The basic design considerations for stills are discussed. In a review of stills, and of their development, their various characteristics are described. Operational pressures are in the millimetres range. Critical remarks on the most suitable operational pressures are added in the last section.

Article by C. A. Lee *Chem. Engng.* 63, July 1956 189-194

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Volatility of Vinyl Plasticisers 152/I

United States. The plasticisers used with vinyl resins may be lost from the compounds during use. The importance of plasticiser vapour pressure on this loss has already been pointed out and the present studies were carried out to investigate the relation between vapour pressure and plasticising loss and to assess the usefulness of various processing and service tests for this loss. The temperatures at which 44 plasticisers had vapour pressures of 0.05 microns and 5.0 microns Hg are given. These have been measured by the high vacuum method of Quackenbos. The temperature for a vapour pressure of 0.05 microns Hg was found to check well with the rated temperature for a given plasticiser in electrical wire insulation compounds. Standard compounds having a composition of Resin (co-polymer of 95% vinyl chloride and 5% vinyl acetate)—100 parts, dibasic lead phosphite—2 parts, dibasic lead stearate—1 to 2 parts, Plasticiser—40 to 70 parts, were made for subsequent testing. The activated carbon test, in which samples of 4-mil film are sandwiched between layers of activated carbon in a 1 pint paint can and their loss in weight after 24 hours at 70°C recorded, is widely used. Plotting the results of this test against vapour pressure of the plasticiser did not give good correlation. It is probably a satisfactory test for rough screening of plasticisers, but small differences in results are not significant. For determining the volatile loss during processing of a plasticised vinyl compound, a test is carried out in which some samples are milled under standard conditions and their weight losses recorded. The results of this test are more closely related to the vapour pressure of the plasticiser than in the previous test and, over a wide range, the milling rate of weight loss, in grams/sq. metre/min., vary linearly with vapour pressure down to a value of the latter of 0.05 mm. Hg. The data from the test are useful in estimating losses during calendering film or sheeting and examples of this are given. Room ageing of 4-mil films for 2½ years gave weight changes having little relation to other tests, apart from the fact that dibutyl phthalate gave the highest weight loss in this and the activated carbon test, and also has the highest vapour pressure. Longer ageing might have given better correlation. For temperatures above room temperature and for rough estimates at room temperature, the equation, developed by Quackenbos from measurements at 98°C and given below, may be used:

$$\text{Life (in hours to lose 10\%)} = \frac{0.08}{\text{vapour pressure (mm. Hg at service temperature)}}$$

Article by W. J. Frissell *Industr. Engng. Chem.* 48, June 1956 1096-1099

Preparation, Properties and Applications of Silicon Monoxide 153/I

Germany. Silicon monoxide was first discovered at the beginning of this century and since then several methods of preparation have been described by various authors. In all cases, SiO_2 is reduced by H_2, C, Si to SiO. Its formation in gaseous or solid form in the reaction can be proved by spectral analysis, x-ray and electron-diffraction examinations. The method given by Grube and Speidel for the preparation of solid SiO has proved the most practical for the laboratory. SiO can be stored, if kept in a dry atmosphere with a low oxygen partial pressure. It has been observed that platinum suffers a melting point depression when SiO is present. A platinum thermocouple, for instance, becomes brittle under such conditions. It seems that the platinum reacts with the SiO to Pt_5Si_2 forming at 830°C an eutectic with platinum. SiO is of industrial interest in metallurgy for purifying metals and its property of having a higher vapour pressure than Si or SiO_2 proves to be an advantage for coating applications and electron microscopy. It has also been found that SiO is transparent to electrons and layers made of it show no structure. It is suitable therefore as a support for specimens and for replica preparations in electron metallography as it improves the resolution obtainable. Its low evaporation temperature is of particular advantage where these layers or replicas are produced by evaporation in a high vacuum. Its acid resistance makes it possible to dissolve the metal base away thus giving a faithful replica of the structural

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Article by D. Schulze *Chem. Technik* **8**, June 1956 341-346

details of the specimen surface. Because of its mechanical and thermal properties, it can be used as a standard of comparison for magnification and truth of reproduction quality in electron microscopy and it can also be used for electron-optical high temperature investigations. Thin films of Si0 changing in air to SiO_2 are of considerable mechanical stability and are frequently used to protect bloomed lenses, etc.

154/I

Semi-Quantitative Spectrochemical Analysis of Silicon

Article by P. H. Keck, A. L. MacDonald & T. W. Mellichamp *Analyt. Chem.* **28**, June 1956 995-996

United States. By conventional spectrochemical methods, the limits for detection of impurities in high purity silicon are: For Al–1, Ca–1, Cu–1, Mg–1, Ti–10, and Zn–10 p.p.m. by weight. In using a method of concentration by vacuum distillation, these limits are reducible to 0.01, 0.01, 0.01, 0.01, 0.1, and 0.1 p.p.m. respectively. The method represents a preferential evaporation of impurities, and consists in melting the silicon by high frequency induction using the floating zone technique. This causes some of the silicon to be evaporated and deposited on a quartz tube. Spectrochemical analysis of the deposit reveals the presence of impurities not detectable in the original silicon. The maximum concentration factor is the ratio of the weight of the distillate that contains the impurities and the weights of the molten bead from which the impurities originated.

155/I

The Surface Areas of Evaporated Metal Films

See Abstract No.: 55/III

156/I

Semiconductivity and Catalysis in the Nickel Oxide System

Article by T. J. Gray & P. W. Darby *J. Phys. Chem.* **60**, Feb. 1956 209-217

United States. The relationship between catalytic activity and the defect solid state is now widely accepted. Interest has been focused, mainly, on the variation of semiconductivity during adsorption, desorption or reaction of gases on a solid surface. Using, substantially, the method of Gray (*Nature*, **162**, 260 (1948)) these relationships have been investigated for nickel oxide. Following the deposition of a thin nickel film by controlled vacuum evaporation and subsequent oxidation of the film, measurements were made of the change in conductivity with temperature (*1*) after evacuation at the oxidising temperature, (*2*) in the presence of oxygen at a pressure of 10^{-2} to 10^{-1} mm. Hg and (*3*) when reduced by limited amounts of either hydrogen or carbon monoxide. The increase of the conductance observed with adsorption of oxygen is typical of a *p*-type semiconductor and at 295°C and 6×10^{-2} mm. Hg the kinetics of the process are essentially linear. At lower temperatures and pressures an initial second order process occurs at the start of adsorption, giving way to a first order process as adsorption continues. This behaviour is typical of all oxides so far investigated. The rate of adsorption varies with pressure, at constant temperature, indicating a saturation of the effective sites with oxygen, Determinations of the first order velocity constant have been made for a series of adsorptions on a film of constant activity and a value of 32 kcal/mole was obtained for the apparent activation energy. In desorption, a second order process occurs. The rate of desorption at a given temperature is a function of the operational pressure. Below 295°C the desorption is extremely slow, with an apparent activation energy of the order of 60 kcal/mole. If the oxygen used in adsorption is atomised or ionised, say by a discharge, a rapid increase in conductivity occurs. This conductivity falls and the normal rate of adsorption is resumed after the discharge is stopped. Hydrogen and carbon monoxide are adsorbed irreversibly on to the Ni0 with an initial fall in the conductivity. If hydrogen and oxygen react together over the surface and the product is continuously removed by a liquid oxygen trap, the apparent reaction order is one-half and the activation energy −3.4 kcal/mole in the range 0–137°C. The rate of reaction is independent of hydrogen partial pressure and proportional to the square root of the oxygen partial pressure. When oxygen is present in excess of stoichiometry the reaction is apparently zero order. The reaction $2C0+0_2 \rightarrow 2C0_2$ has been studied from 200 to 300°C. If an excess of oxygen is used in the gas mixture the conductivity falls initially but rises beyond its original values as oxygen is adsorbed following the oxidation of C0. The order of reaction is one-half and an apparent activation energy of 20 kcal/mole was obtained. In the discussion the authors state that the activation energy required to produce a positive hole from the defect structure can be derived from the temperature coefficient of the conduction process according to a formula given in the article. Previous workers have not emphasised sufficiently the effect of the previous history of the sample on activation energy values. From the results obtained it is concluded that in nickel oxide, free from foreign impurities, the activation energy is due to a single-type-impurity conduction and will be between 1.25 and 2 ev for stoichiometric Ni0. The structure-sensitive low temperature activation energy is a composite of a constant activation energy for the bulk material modified by an activation energy for the surface zone dependent upon experimental conditions.

157/I

Chemical Analysis of Thin Films by X-Ray Emission Spectrography

United States. Difficulties in handling microgram samples by classical micro-analysis has limited the work done on the chemical analysis of surface films, residues and corrosion products. Some work, to which references are given, has been accomplished, but the methods are time consuming and of limited application. X-ray emission spectroscopy has been investigated as a possible method of analysis and found capable of measuring surface densities in the range, 1 to 100×10^{-6} g./sq.cm. to within 2% for iron, nickel and chromium. The fluorescent x-radiation excited in the sample is very small, so great care must be taken in reducing the background count. Mylar substrates were used for the films, because of the high strength and low scattering power of thin (0.00025 inch) sections of the material. A North American Philips plane crystal spectrograph with a Machlett OEG–50 tungsten target tube, a Soller blade collimator, a lithium fluoride analysing crystal and a North American

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Philips A.62019 argon-filled Geiger tube formed the spectrographic system. Fixed-angle counts at the proper Bragg setting were made, the 1st order Kα lines being scaled for all elements except molybdenum and niobium, when the Lα lines were measured. Experimental films of pure metals and stainless steels were vacuum evaporated on to the Mylar film. Different-thickness oxide films were prepared by oxidising metal films reinforced with Formvar in a 5.0% nitric acid– 0.5% potassium dichromate bath at 60°C for different times and then dissolving away first the metal and then the Formvar. An anhydrous 1% bromine-methanol mixture in an inert atmosphere was used for stripping from the metal. Films were also obtained from metal coupons and three variations of the stripping technique were used to determine whether the sample consisted of film and inclusions, fragmented oxide film or large sections of film. 4 to 6 sq.cm. samples were taken. Scaling was done for a fixed time to yield a probable counting error of 1%. When the counting time exceeded 2 minutes, redeterminations of the background rate were made every 2 minutes. 1.0±5% counts/sec., corrected for background could be measured. For metal and alloy samples of varying thicknesses and for oxide films, the number of counts/sec. was found to be proportional to the surface density of the metal in μg./sq.cm. Deviations from this proportionality are small and are in good agreement with those calculated by Noakes (*ASTM Spec. Bull.* **157**, 57 (1954)). All deviations observed on samples up to 100 μg./sq.cm. fall within the chemical microanalysis error of ±5%. A table, partly reproduced below, gives a comparison of x-ray and chemical analytical data for films of austenitic stainless steels and for oxide films isolated from their surfaces.

Sample size, 25 to 100γ

Nature of Film Sample	*Analytical Method*	*Fe*		*Cr*		*Ni*		*Si*		*Nb*		*Mo*	
		%*	*Std. dev.*	%	*Std. dev.*	%	*Std. dev.*	%	*Std. dev.*	%	*Std. dev.*	%	*Std. dev.*
Type 304 alloy	X-ray	70.5	0.5	20.2	0.2	8.7	0.1	—	—	—	—	—	—
thickness, 300 Å	Chemical	69.6	1.2	20.6	0.7	9.0	0.1	1.0	0.1	—	—	—	—
Type 316 alloy	X-ray	69.5	1.0	19.4	0.2	11.3	0.1	—	—	—	—	7.2	0.4
thickness, 300 Å	Chemical	68.5	1.8	19.6	0.3	10.9	0.2	1.2	0.1	—	—	0.4	0.7
Type 304 oxide-1	X-ray	37.2	4.0	13.4	2.0	9.4	1.2	—	—	—	—	—	—
thickness, 30 Å	Chemical	34.0	3.1	14.0	3.4	10.7	4.0	9.9	2.0	—	—	—	—
Type 316 oxide-1	X-ray	42.1	3.2	12.6	0.7	4.9	0.6	—	—	—	—	(1.2)	—
thickness, 30 Å	Chemical	45.0	4.2	13.0	2.0	5.4	2.1	14.5	3.2	—	—	4.2	1.1
Type 304 oxide-2	X-ray	15.0	2.0	4.55	3.7	3.8	0.2	—	—	—	—	—	—
thickness, 300 Å	Chemical	15.1	2.6	46.6	5.0	4.0	0.5	3.3	0.1	—	—	—	—
Type 316 oxide-2	X-ray	25.0	3.2	36.8	3.1	5.0	0.3	—	—	—	—	(0.2)	—
thickness, 300 Å	Chemical	25.2	4.0	36.1	4.3	5.2	0.8	4.0	0.3	—	—	1.6	0.3

* Per cent by weight.

Article by T. N. Rhodin *Analyt. Chem.* 27, Dec. 1955 1857-1861

Determination of the Oxide Film Thickness on Tin

158/I

United Kingdom. Information was required on the thickness of the natural oxide film formed on tin (or tinplate) in connection with work on corrosion of tin in anaerobic fruit acids. The electrometric reduction method, which is described, was previously believed to be only applicable to metals more electronegative than hydrogen, but was found to work with tin because of its high hydrogen overpotential. A test surface (the flat end face of a 1 cm. diameter cylinder) was prepared from AR tin, polished, stipped of oxide by treatment with HCl or by electrolytic reduction, and then allowed to stand in dry air for a definite period. The remainder was then protected with a coating of cellulose lacquer and the cylinder placed in one limb of a *H*-cell containing N/100 KCl solution, with a Pt anode in the other limb. The two limbs were separated by a porosity–4 sintered-glass diaphragm, the electrolytic being initially placed in the anode limb only. The apparatus was evacuated and N_2 bubbled through the electrolyte to remove O_2; the apparatus was then evacuated again and refilled with N_2, after which the electrolyte was forced by nitrogen pressure through the diaphragm into the limb containing the tin specimen. The oxide layer (assumed to be stannous) was then reduced by cathodic polarisation (6μA/cm².) and the potential of the tin measured at frequent intervals against a Ag-AgCl electrode. Graphs of this potential against time show a sharp drop when reduction is complete, and the quantity of oxide removed is calculated from the quantity of electricity used, the area of the film and the density (taken as 6.3). The film thickness formed after standing 1 hr. in dry air was estimated at 14–15 Å, after standing 19 hr. at 18–20Å.

Letter by F. W. Salt & J. G. N. Thomas *Nature* 178, 25.8.1956 434-435

The Adsorption of Some Organic Vapours by Wool and Nylon

159/I

See Abstract No.: 4/IV

The Dyeing of Cellulose Acetate with Non-Ionic Dyes III. Dyeing from the Vapour Phase

160/I

United Kingdom. A study has been made of the absorption from the vapour phase, by seconday cellulose acetate, of five model dyes. These are *p*-nitroaniline, *N N'*-dimethyl-*p*-nitroaniline, azobenzene, *p*-aminoazobenzene, and *N N'*-dimethyl-*p*-aminoazobenzene. The amounts absorbed at equilibrium have been measured, and their

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dependence on the vapour pressure of the dyes and the temperature of the substrate has been established. The vapour pressures of the dyes have been measured over a range of temperatures, those of azobenzene by manometry and the remainder by Knudsen's effusion method. The results together with the absorption data yield absorption isotherms from which are derived the isosteric heats of absorption of the dyes on cellulose acetate. The values, in the above order, are as follows −21.2, −21.4, −17.8, −22.0, and −22.7 kcal./mole. The vapour pressure data are also used to evaluate the heats of vaporisation or sublimation of the dyes. These heats are applied to aqueous dyeing data already published to derive the absolute heats of association of the dyes on cellulose acetate. The results are in substantial agreement with the heats of absorption of the vaporised dyes. A brief study has been made of the absorption by nylon and Terylene of vaporised azobenzene. The results for nylon yield a value for the heat of absorption of −18.0 kcal./mole. The results for Terylene are insufficiently complete for quantitative treatment.

(*Author*)

Article by T. G. Majury *J. Soc. Dyers & Colourists* **72**, Feb. 1956 41-49

161/I **A Corrosion-Resistant High Vacuum Valve for Liquids**

See Abstract No.: 15/I

162/I **Apparatus for the Anaerobic Filling of Phials**

United Kingdom. The device described is designed to permit the introduction into a phial of a known volume of solution, the process being carried out in a vacuum. The solvent and solute are isolated by magnetically operated break seals inside an evacuated glass system and are distilled in turn into a third bulb of the system. A narrow glass tube passes from the top of the burette through the wall of this bulb and has an open end inside and at the bottom of the bulb. The distilling line is sealed off by glass blowing after the liquids have reached the third bulb and the contents of this vessel are then forced through the connecting tube into the burette by the vapour pressure increase produced by gentle heating. The burette is graduated in 0.1 ml. and its lower end is connected by a specially designed valve, (described in *Chem. & Industr.*, 1956, 569), to the phial manifold. The manifold is evacuated and flamed and then closed off from the pump by a dry valve of the cone-and-socket type, operated by a solenoid. Each phial is in turn surrounded by liquid air and on each occasion the burette valve is opened. The liquid then condenses in the cooled phial and the latter is sealed off under vacuum when it contains the volume. A table shows the ratio of the titre to the volume of the phial contents to be virtually constant in a case where 7 phials were filled with a solution of trifluoroacetic acid in hexane according to the method described. Advantages of the device are that all soluble tap greases etc. are excluded and the operation can be carried out at a filling rate of 25 phials per hr.

Article by R. H. Biddulph & P. H. Plesch *Chem. & Industr.* 30.6.1956 567

163/I **Electrode for Measuring the Conductivities of Solutions at Low Pressures**

United Kingdom. In connection with a study of the rate of solution of salts at low pressures an electrode was designed capable of measuring changing conductivities of salt solutions at 10^{-1} mm. Hg. The electrode consists essentially of a glass tube, ending at the top in a B.19 standard ground glass cone for connection to a round-bottomed flask of, say, 1 litre volume. A cork, grooved to take the two main wire leads, fits into a specially provided glass collar at the top. The wire leads, encased in a 3-mm. diameter tube each, pass down the glass envelope and are joined to glass-encased copper wires, sealed into the envelope by means of a glass-to-metal seal, about 30 mm. from the bottom. The latter join two platinum foil electrodes placed on the outside of the tube. The overall length of the assembly is 100 mm. In operation, the electrode is mounted in the flask and the flask is evacuated to the desired pressure. The electrode cell constant was found to be 2.39.

Note by R. C. Braun *J. Sci. Instrum.* **32**, Dec. 1955 489-490

164/I **Method of Degassing Liquids**

See Abstract No.: 166/III

165/I **Gas Counting Technique in Biochemistry II.**

See Abstract No.: 7/IV

166/I **The Determination of Tritium in Tritiated Water**

See Abstract No.: 8/IV

167/I **Rapid and Precise Measurements of Moisture in Biological Materials**

United States. A moisture determination apparatus is described which is similar to the instrument communicated by Anderson and another described by Beckett (*Biological Applications of Freezing and Drying*, R. J. C. Harris, 1954, 285). The instrument is claimed to be fast and precise because the water is measured manometrically and the sample under test is never exposed to the atmosphere. The essential parts of the apparatus are a condenser, an Octoil-S oil-filled manometer, a sample container and an interchangeable expansion chamber. The

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manometer gives the vapour pressure of the water and since the pressure is directly proportional to the amount of water and inversely proportional to the volume of the vapour, the apparatus is calibrated simply by measuring its volume. A formula is given for the calculation of the amount or weight of water for a given pressure. Details are given of the procedure to degas the manometer oil and of the steps involved in operating the apparatus. A special feature of the particular apparatus is the fact that the manometer oil can be degassed *in situ*, that the manometer can neither penetrate into the pump nor into the apparatus and that the manometer is sufficient to check the operation of the instrument obviating the use of a separate vacuum gauge.

Article by R. J. Heckly *Science* **122**, 12.10.55 760-761

The Micro-Determination of Residual Moisture in Freeze-Dried Biological Materials. 168/I

United Kingdom. A micro-drying method is described, which is simple, rapid and reproducible. It has been shown to give results in reasonable agreement with the Karl Fischer method, and with the vapour-pressure method. The results on samples of low moisture content are, however, considerably higher than those by the so-called American standard method. The method has been in routine use for over 3 years.

(Author)

Article by P. R. W. Baker *J. Hygiene* **53**, Dec. 1955 426-435

Freeze-Drying V. Freeze-Drying as a Large-Scale Operation 169/I

See Abstract No.: 38/IV

An Experimental Comparison of Freeze-Dried and Frozen Cortical Bone-Graft Healing 170/I

United States. Earlier work by Kreuz, Hyatt, Turner and Bassett, compared the healing of fresh autogenous, frozen and freeze-dried bone grafts in dogs. Freeze-dried and frozen cortical bone grafts were found to heal in the same manner as fresh autogenous grafts, but slightly slower. Initially, the freeze-dried grafts healed slightly faster than frozen grafts. Since that work was undertaken improvements have been made in the freeze drying technique used at the U.S. Naval Medical Research Institute, resulting in an improvement in freeze-dried bone graft healing. In experiments to evaluate the effect of cathode-ray sterilisation of frozen and freeze-dried bone grafts, the non-irradiated controls were examined to re-assess the difference between freeze-dried and frozen grafts. Rectangular cortical bone grafts from mongrel dogs obtained at sterile autopsy were divided in half and preserved by freezing at −78°C or freeze-drying. Owing to refrigerant failure, the frozen grafts were not kept as long as the others and were implanted as bilateral homogenous inlay grafts in the radii of adult mongrel dogs. The dogs were sacrificed after 35 or 90 days as these time had proved best for observing initial and maximal bone revascularisation previously. A 0.3 to 1 cm. cross section was taken from the centre of each graft and these blocks fixed in buffered formalin solution, electrolytically decalcified and routine hematoxylin and eosin sections 10 μ thick prepared. Three independent investigators evaluated the graft healing in these sections, without previous knowledge of their origin, according to an arbitrary scale. The results of some of the experiments are given in a table reproduced below. From an over-all standpoint freeze-dried grafts performed better than frozen grafts at 90 days by a ratio of 1.63 to 1.

Evaluation of Frozen as Compared with Freeze-dried Grafts

90-Day Grafts.
Based on Ten Frozen and Ten Freeze-Dried Grafts.

	Stage of Healing	*Perivascular New Bone*	*Amount of Residual Graft*	*Total Amount of Graft Present in 10 Grafts Originally*	*Amount of Graft Eliminated*
F (frozen) grafts	23½	15½	29½	40	10½
FD (freeze-dried grafts	28	25½	13	40	27
Ratio of performance F/FD	84%	60.8%			39%
Over-all ratio of F/FD performance (average of above ratios)					61.3% or 1 to 1.63

Article by T. C. Turner, C. A. L. Bassett, J. W. Pate & P. N. Sawyer *J. Bone & Joint Surgery* **37A**, Dec. 1955 1197-1205

Freeze Drying Part III. The Preservation of Micro-Organisms 171/I

See Abstract No.: 24/IV

What is a Virus? 172/I

United Kingdom. The chief discoveries leading to the present-day knowledge of plant, insect and animal viruses are reviewed. Characteristics of viruses in general are that they are extremely small, infectious and require a living cell in which to propagate. The first virus to be crystallised was the tobacco mosaic virus in

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1935. This has since been found to be a nucleoprotein containing 6% ribose nucleic acid and 94% protein. It is possible to remove the acid component from one sample of this virus and the protein from another and then re-combine the two constituents to form an active virus. X-ray studies showed in 1936 that the tobacco mosaic virus had a rod-shaped structure. Since then electron microscopy has confirmed that this virus is a long, comparatively rigid rod with a thread of nucleic acid running through the centre of the rod. The virus cannot multiply without the nucleic acid. Other plant viruses which have been crystallised include the tomato bushy stunt, tobacco necrosis and turnip yellow mosaic. All are nucleoprotein containing ribose nucleic acid but their structures are different. Plant viruses may be spread by contact or by insects, in which the viruses can live and multiply. Leaf hoppers bred from an infected female have contained active viruses after 21 generations which had no access to infected material. Viruses which are known to attack insects are grouped into three types according to whether they occur in crystals or granules in the diseased tissue or freely in the insect. Some of these viruses multiply inside the cell nuclei. New microtome techniques have made it possible to make thin sections of the diseased cells and also of the viruses themselves for study in the electron microscope. Micrographs of the infected blood cell of a fly larva and of the virus causing the infection are shown. The magnifications used were ×25,000 and ×92,500 respectively. In the higher animals viruses are responsible for foot and mouth disease and for poliomyelitis. The virus of the latter has recently been crystallised with retention of its infective power. Some workers believe that there may be a connection between viruses and cancer. This view has been supported by work on the viruses of rabbit-papilloma and avian leukosis which have now been isolated and photographed with the electron microscope. Mammary cancer in mice has been found to be due to a typical virus.

Article by K. M. Smith *Times Sci. Rev.* Spring 1956 3, 3-6

173/I **Freeze-Dried B.C.G. Vaccine. Methods Adopted in Preparation of a Standard Product**

See Abstract No.: 29/IV

174/I **Freeze-Dried B.C.G. Vaccination of Newborn Infants with a British Vaccine**

United Kingdom. In a recent Medical Research Council trial of B.C.G. and vole bacillus vaccine on children at school leaving age, it was shown that protection was offered by these vaccines against tuberculosis for the children of this country at the present time. However it was found that 40% of these children had already had their primary infection and, as the most significant periods of risk of tuberculosis infection are in earliest infancy and puberty, it is desirable that vaccination takes place in infancy. The risk of genital tuberculosis of girls in puberty makes their vaccination in infancy desirable. Though it has been shown that infants can be safely vaccinated with B.C.G., its period of protection has not yet been determined. Five years after the vaccination of newborn infants with Danish vaccine only seven in over one thousand reverted and required revaccination. The sensitivity of the others had scarcely decreased. Not only must the vaccine used provide adequate antigenic potency, but it must also produce no complications. Vole bacillus vaccine is unsuitable for infants; doses which do not produce tubercolin conversion in some infants, produce complications in others. These complications last for a long time and may appear up to 2 years after vaccination. Swedish vaccine and French freeze-dried products are too weak and for the past three years, a dose of 0.0375 mg. of fresh Danish B.C.G. vaccine has been used for infants. This has the disadvantages associated with any liquid vaccine, but complications are of the order of less than 0.3%. However, over the past 18 months, a freeze-dried preparation from the Glaxo laboratories has been investigated. Prepared by the method of Ungar, Farmer and Muggleton (*Brit. Med. J.* Sept 8th, 1956 1956, 568), it is free of the clumping experienced during the reconstitution of other freeze-dried vaccines making the determination of the number of viable organisms and the ensuring of a consistency uniform dose difficult. The vaccine was resuspended to contain 10,000, 120,000 and 1,000,000 viable organisms in 0.1 ml. and was injected intradermally. 10,000 viable baccilli per dose was found to be antigenically inadequate and the 1,000,000 bacilli dose, slightly more potent than the Danish B.C.G., tending to produce lesions at the site of inocculation and to cause glandular complications. The 120,000 bacilli dose, though slightly less antigenic than the Danish vaccine, has given comparable results to that vaccine and, so far, has produced no complications. This is therefore taken as the optimal dose. The accuracy of bacillary dosage now possible, coupled with the advantages of a dried vaccine, make it possible that the liquid preparations may be replaced by freeze-dried vaccines in the near future.

Article by M. I. Griffiths & W. Gaisford *Brit. Med. J.* 8.9.1956 565-568

175/I **Carzinophilin**

Japan. This antibiotic, which, while inactive against Gram-positive bacteria generally, has shown activity against Gram-negative forms and Yoshida sarcoma cells, is produced from *Streptomyces sahachirai*. In fermentation experiments, *S. sahachirai* is grown in a medium containing glucose, peptone, dry yeast, malt extract, salt, urea and chalk. The activity can be extracted from the filtered broth at 0–5°C and a *p*H of 6 to 6.5 with either chloroform, benzene or butyl, ethyl or amyl acetate and then extracted with water at a *p*H of 9 to 10. The aqueous layer is freeze-dried after repeating this procedure, to produce an active white powder. Carzinophilin is an unstable acid which forms stable salts. Nobukatsu Shimada (*J. of Antibiotics (Tokyo)* 1955, **8**, (3) 67-76) has described clinical tests showing its remarkable efficacy in the treatment of malignant neoplasms.

Note by P. B. Dickenson *Mfg. Chem.* 27, April 1956 140

176/I **Possible Cation-Carrier Substances in Blood**

United States. It has been postulated that the transport of specific ions across cellular membranes may be achieved by carrier molecules. In the case of the red cell, such carriers would form lipide soluble complexes with

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Na or K ions, and these complexes should be non-dissociable in lipide but dissociable in water solution. Some support has been given to these theories by investigations concerning the extraction from blood of such a lipide-soluble material. Both human blood and plasma have been used as starting materials. Samples of whole blood were incubated at 37°C with radioactive potassium-42 for one hour or more. After incubation the blood was frozen and dried under vacuum. Aliquots of the dried material were then extracted with a number of organic solvents, and the amount of potassium extracted was determined. The most effective solvent by far was a hot 2:1 chloroform-methanol mixture. This extracted 0.532 m.moles of K-42 per litre of blood and 0.221 m.moles/l. plasma. The solubility of inorganic potassium was found to be 0.0008 m.mole/l. by drying and extracting a buffer which simulated the ionic composition of plasma. It was also shown that the chloroform-soluble material gave up the cation to water, but subsequent shaking of the water solution with fresh chloroform did not result in K-42 being taken up by the chloroform. Thus the material extracted from blood and plasma shows the characteristics postulated for the cation-carrier substance. It seems likely that the material is lipide in character, and possibly contains phosphatides, since these may be shown to act in a similar manner.

Article by A. K. Solomon, F. Lionetti & P. F. Curran *Nature* 178, 15.9.1956 582-583

Small Angle X-Ray Diffraction Unit 177/I

See Abstract No.: 50/II

Multiple Target Nuclear Magnetic Resonance Cryostat 178/I

See Abstract No.: 119/II

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17 — METALLURGY — 17

Trends on Metallurgical Research in the United States 179/I

See Abstract No.: 39/I

Technical Developments of 1955 180/I

United States. An annual review of developments in Metal Finishing dealing with the subject under the following headings: Cleaning; Pickling; Polishing; Aluminium Plating and Anodising; Metallic Coatings; Conversion Films—Corrosion Preventatives; Testing and Control; Waste Treatment and Metallising—Vacuum and Vapour Processes. Under the latter heading an article by Weil (*Bull. Inst. Mer. Fin.*, 5, 169) is quoted which contains a detailed explanation of the mechanism of film formation, and two patents, one claiming a carbide wick element for evaporating aluminium (*U.S. Pat.* No. 2,703,334) and the other a process for applying first copper, then silver to non-conductors (*U.S. Pat.* No. 2,719,079). 366 References.

Article by N. Hall *Metal Finish* 54, Jan. 1956 43-52

New Horizons in Foundry Progress 181/I

United States. Future developments can be expected in a number of inter-related fields concerned with foundry progress. Firstly, there will be a growth in production of the unexploited metals. Only about 25 of the 70 known metals are produced in commercial quantities at present. Secondly, metals currently in use will be developed in forms having improved properties, such as better resistance to corrosion and wear, and greater tensile strength and uniformity. Those improvements will be made possible partly through new processesing methods, *e.g.* vacuum melting and partly through a closer study of the effect of minute additions. Some recent results of the latter work are: The maximum size of a steel component that can be hardened thoroughly is considerably increased by the addition of boron. Adding bismuth larger white iron castings can be produced. The life expectancy of resistance wire is raised by adding small amounts of calcium. Large-scale application of the controlled addition of small amounts of such metals will call for techniques ensuring uniform distribution of the impurities and precision analysis, for which the use of radioactive tracers may be an especially effective tool. Vacuum degassing of metals results in sound non-porous castings of increased strength if due attention is given to 'directional solidification'. No diffusion pumps are required and the equipment used need not be expensive. Other foundry practices discussed are high pressure moulding and shell moulding. The carbon dioxide process for hardening moulds and cores without the application of external heat should prove to be one of the most significant developments of the decade. This process depends upon binding the sand grains together by a silicic acid skeleton liberated *in situ* through the interaction of carbon dioxide and waterglass. The process is claimed to be cheap due to the absence of expensive binders and the need for core and mould drying. A new process, known as core 'shooting', minimises some of the problems of venting and the need for special sands. Economies in material will develop out of fundamental research into fluid flow applied to the flow of air and metal

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within the mould cavity. This work will bring about a reduction in the number of rejects due to dross or air entrapment. A table reproduced below, gives an estimate of the trends in production of aluminium castings.

	Percent of Total Production		
	1952	1954	*Est.* 1960
Die Castings	32	38	44
Permanent Mould	28	35	41
Sand Castings	38	25	14
Centrifugal, precision investment, shell moulding plaster mould, frozen mercury, etc.	2	2	1

Article by H. J. Heine *Bull. School Mines Metall. Univ. Missouri* No. 91, 1956 1-14

182/I

Powder Metallurgy Reviewed

United Kingdom. Powder metallurgy may be used for one or more of three basic reasons: to avoid the high temperatures necessary to melt certain metals such as tungsten, molybdenum and tantalum; to obtain special properties such as controlled grain size or porosity; and to give an economic method of producing large quantities of a single component, as in the manufacture of parts from sintered-iron powder. Powders are generally prepared by the reduction of the metal oxide. They are pressed in a mould to give a compact which can be handled and subsequently heat-treated to fuse or 'sinter' the material. In this way the mass of powder is transformed into a dense, metallic powder, although at no stage does the whole mass become molten. Sintering must be carried out in a non-oxidising atmosphere, *e.g.* in a hydrogen or vacuum furnace. In the case of a single metal the sintering mechanism is a gradual diffusion at the boundaries between individual powder particles. A similar process takes place in the sintering of alloys provided no liquid phase is formed. In certain systems a low melting point eutectic may be formed and some liquid phase occurs which cements the particles together. Molybdenum is produced by powder metallurgy to overcome the disadvantages of coarse grain size and poor hot working properties associated with arc-melted molybdenum. The sintered bars can be hot swaged or hot hammered to rods or slabs. Rods are used in the manufacture of wire and the slabs are hot rolled down to 0.06 inch and then cold rolled to finished sheets. Sintering, reheating and annealing are carried out in hydrogen-atmosphere furnaces. The cemented carbides illustrate the use of powder metallurgy to give a special metallurgical structure. These may consist of tungsten carbide bonded with cobalt or a mixture of tungsten, titanium and tantalum carbides, again bonded with cobalt. Titanium and tantalum carbides are produced by the reduction of the oxides by carbon in a vacuum furnace. High temperatures of the order of 2,000°C are required. Sintering furnaces for carbides may be either continuous-type hydrogen furnaces using a molybdenum winding, or high-vacuum high-frequency induction, batch-type furnaces. Powder metallurgy makes it possible to study all the stable carbides borides and silicides of metals. A new development is the fabrication of beryllium by powder metallurgy. Beryllium ingots can be cast successfully in a vacuum induction furnace, but the resulting metal is difficult to work. By mechanically reducing the ingots to a powder which is pressed and sintered at about 1,100°C it is possible to obtain metal with a fine grain structure and good mechanical properties.

Article by L. D. Brownlee *Engineering* 14.9.1956 331-332

183/I

Economics of Investment-Cast Vacuum Alloys

United States. Details are given of development work on a vacuum investment casting method employing an air-melted base alloy as the charge and making the additions to the base alloy, such as boron, aluminium or titanium, through a lock chamber of the vacuum furnace. The advantages of using an air-melted base alloy are that high purity raw materials can be used with little regard to gas content, and that the gas content of the charge is known and consistent. This leads to a considerable reduction in (vacuum) melting time. The Cannon-Muskegon Corporation operate such a furnace. It has a 400-lb. capacity and includes a 3-ft. diameter mould table rotated, through a vacuum seal, at up to 800 r.p.m. for centrifugal casting. A second process of investment casting has also been developed which operates by remelting vacuum alloys. This eliminates much of the accessory equipment necessary in the original method, since no additions are required and is therefore cheaper to operate. A 50-lb. furnace has been developed for this process giving 6.9 moulds per hour. Pressure can be reduced to 10 micron Hg in 3–4 minutes. The cast of the furnace is about $15,000 exclusive of power supply. Vacuum investment castings by the vacuum re-melt method can be produced at under twice the price of air-melted castings. Development in this field should soon reach a stage where, with the development of low-cost furnaces and cheaper base-alloys, vacuum investment castings will be less than 30% more costly than air melted castings.

Article by F. K. Iverson *P.M.M.* 14, June 1956 130-135

184/I

Investment Casting of Vacuum Alloys

See Abstract No.: 127/III

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Vacuum and Controlled Atmosphere Furnace for High Temperature Heat Treatment

185/I

Sweden. Increasingly stringent requirements on magnetically soft materials have made the design of heat treating furnaces for these materials more and more difficult. Elevated and accurately controlled temperatures, high vacuum and an extremely pure controlled atmosphere are essential. Good results have been achieved with an entirely new type of furnace. The article describes the furnace itself, its maintenance and its operation.

(*Authors*)

Article by E. Edman & A. Victor *ASEA Journal* **28**, 1955 84-96

Improvements i.o.r.t. the Melting and Casting of High Melting Point Metals or Alloys

186/I

See Abstract No.: 91/III

Apparatus for Melting Highly Reactive Metals

187/I

See Abstract No.: 103/III

Controlled Atmosphere Melting of Magnetic Materials

188/I

See Abstract No.: 100/III

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Melting of High-Purity Uranium

189/I

United States. A process is reported for the preparation of uranium metal at a degree of purity as is required for the study of the fundamental properties of uranium. Electrolytic uranium is first prepared by fused salt electrolysis. This contains large quantities of potassium and lithium from the electrolyte and small quantities of heavy metals and carbon. Much research was required to develop a technique to reduce contamination (mainly by carbon but also by iron, copper and silicon) during the melting into ingots. Very thorough cleansing with nitric acid, and washing (including 48 hr. in running water) is used to remove potassium and lithium followed by vacuum drying of the metal crystals. The pure, dry uranium crystals are then compacted under argon and placed in the crucible which is quickly transferred to the furnace for immediate evacuation. Vacuum melting is essential to remove the large quantities of gas contained in the electrolytic crystals: Although an inert atmosphere would appear to prevent contamination lithium and potassium removal has proved less efficient under such conditions, and the vacuum melted ingot has a cleaner surface. The vacuum system must be able to reduce the pressure below 5×10^{-7} mm. Hg when pumping down from cold and must have a very high pumping speed so that the pressure, which may rise to 10^{-4} mm. Hg during early heating, can be quickly reduced again to the 10^{-6} mm. Hg pressure level. A pumping unit consisting of a mechanical fore pump, booster pump and oil diffusion pump is used in conjunction with a water-cooled baffle and a liquid nitrogen cold trap (specially developed so as not to impair the high pumping speed) to prevent oil diffusing back into the furnace chamber. Resistance heating has been found to be preferable to induction heating, and pure urania the most suitable material for the crucible. When melting is complete the crucible is lowered very slowly into the cold end of the furnace tube, resulting in directional solidification. This solidifying of the metal from the bottom upwards gives a sound ingot, free from shrinkage cavities. Because of the extreme sensitivity of uranium to oxidation, and contamination by carbon, an elaborate procedure is used for the preparation of samples for analysis. These samples are thoroughly cleaned, and dried in a vacuum desicator, taking care, as before, to avoid contamination of the uranium with oil vapours from the vacuum pump. The uranium produced by this method is estimated to be better than 99.993% pure, by weight, is metallographically reasonably free from impurities and has a density of 19.050 $\pm$0.002 g./cm.^{3} which agrees very closely with the calculated theoretical value.

Article by B. Blumenthal *J. Metals* November 1955 2-8

Melting and Fabricating Binary Uranium Alloys

190/I

United States. Alloys of uranium with molybdenum, columbium and silicon have been produced in the form of sound, homogeneous ingots up to 4 inch. in diameter and about 50 lbs. wt. This has been achieved by a duplex melting technique which combines vacuum induction melting and consumable-electrode arc melting. Alloys of uranium with molybdenum and with columbium have been successfully fabricated by extrusion, forging, rolling and swaging. Only extrusion has worked satisfactorily for the silicon alloy. The vacuum induction melting furnace consists of a Micarta tube, with stainless steel head and bottom mould container. All three parts are water-cooled. The Micarta tube is 24 inch. long and has a usable inside diameter of 8½ inch. The stainless steel head provides for the vacuum port, sight port and vacuum gauges. The furnace is separated from the vacuum system by a 6 inch, quarter swing valve. The fore pump is a Kinney mechanical pump. The high-vacuum system consists of a liquid nitrogen trap, a booster pump, and a second mechanical pump. A pressure of 0.03 μ Hg is attained on pumping in the cold. With a 50-lb. charge at 1,500°C, pressures of 1–3 μ Hg are obtained. The furnace design is adaptable so that casting may be made in graphite or water-cooled copper moulds. The consumable-electrode arc melting furnace presents no outstanding features, and is of the type now widely used. A report is given of the melting of three uranium alloys, namely (*a*) U with 3.8% Si, (*b*) U with 10% Cb, (*c*) U with 12% Mo. The U/Si alloy has been melted in beryllia crucibles, which have a life of about four melts. At the alloying temperature of 1,600°C the vacuum is about 4 micron Hg. The ingots obtained have been consumable arc re-melted as electrodes 25 inch. $\times$ 1¼ inch in an atmosphere of 50/50 He/A at 20 inch. Hg. A re-melted ingot of 2.5/16 inch diam. is obtained in about 10 mins. Chemical analysis showed good homogeneity.

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Similar methods have been used with U/Cb alloy, for which beryllia-coated graphite crucibles have been more extensively used. This less expensive method gives an alloy with 300 p.p.m. carbon. The U/Mo alloy has been melted and cast in large quantities. Zirconia-coated graphite is used for crucibles and moulds, the more costly and toxic beryllia being used only above 1,550°C. The U/Mo melt is superheated to 1,480°C and held for 15 min. at 1 μ Hg, then cast into 2 inch. diam. split graphite moulds. These castings are consumably remelted to 4 inch. diam. ingots. U/Mo alloys have been fabricated most successfully by hot working, especially by extrusion. Hot rolling and extrusion has been carried out on U/Cb alloys. Little work has been done on fabrication of U/Si alloys, and only extrusion after annealing has met with any success.

Article by F. R. Lorenz W. B. Haynes *J. Metals* 8, August 1956 1076-1080

191/I

The Production of High Purity Vanadium Metal

United Kingdom. A survey of the methods used up to 1948 for the preparation of vanadium and other refractory metals, suggested that the reduction of a suitable chloride by magnesium should form a sound basis on which to develop a process for the technical scale extraction of high-purity vanadium. Vanadium tetrachloride proved unsuitable because of its instability and the difficulty of eliminating the oxytrichloride in a practicable manner. The trichloride, however, was more promising. 80% ferrovanadium was selected as the best commercially available raw material because of its high vanadium and low oxygen contents and ease of chlorination. Elimination of ferric chloride from the vanadium tetra- and oxytri-chloride produced during chlorination is accomplished in a simple manner. The tetrachloride is converted to the trichloride by heating under reflux in a stream of a carrier gas. At the end of the reaction the oxytrichloride is distilled off. The pure trichloride is reduced by magnesium at temperatures not exceeding 850°C in an atmosphere of purified argon. When reduction is complete, the magnesium chloride and excess magnesium are removed from the vanadium sponge first by melting under argon, and then by heating the sponge to 900°C at a pressure of about one micron. A final aqueous leaching may be required to remove the last traces of magnesium chloride. Vanadium metal sponge containing approx. 99.7% vanadium, 0.05–0.2% oxygen, 0.005% nitrogen, 0.01% Hydrogen, 0.01% magnesium and 0.03% iron has been regularly produced in a small unit producing about 3 lb. of metal per batch. Recently a pilot plant producing 40–45 lb. batches of vanadium sponge has been brought into operation.

Paper by E. Foley, M. Ward & A. L. Hock Symposium on Extraction Metallurgy *Inst. Min. Metall.* March 1956

(*Authors*)

192/I

Zirconium—What is its Future?

United States. The low neutron cross-section and high corrosion resistances of zirconium have led to its increasing use in reactor engineering. Work with Sn, Fe, Ni and Cr led to the development of a variety of zircalloys offering a reasonable compromise between highest corrosion resistance and poorer mechanical properties, in building a reactor. A comprehensive table lists commercial suppliers of Zr and Zr products; production methods; specifications; and cost. Arc-melting techniques are most generally used, particularly for tubular, sheet and bar products; powder-metallurgy zirconium has more specialised application. Although not yet in commercial production, electrolytic zirconium powder shows high promise: Vacuum fusion analyses indicate very low impurity content and excellent properties are exhibited in applications involving direct extrusion from the powder. Brief mention is made of work being carried out on cladding fuel elements with Zr and Zr alloys; and the application of a patented process for titanium shape-casting. The latter is a vacuum casting method which is expected to present a relatively inexpensive way of producing complex shapes with high yield. More complete data regarding the effect of impurites on corrosion resistance should permit less rigid quality-control standards: The quality control costs at present amount to two thirds of all the direct labour costs involved in manufacturing the product. The Atomic Commission programme and the development for the nuclear power industry are expected to create a vastly increased demand for zirconium (current reactor designs abroad do not incorporate Zr but, if the trend to higher temperatures is followed, Zr will have to be used). The tremendous losses due to corrosion in the chemical industry suggest another possible future market.

Max. Permissible Sponge Impurities

Element	*Weight %*	*Element*	*Weight %*
Hf	0.01	C	0.02
Al	0.0075	N	0.01
B	0.0001	O	0.10
Cl	0.06	Li	0.0001
Cr	0.010	Rare earths	0.0015
Fe	0.10	P	0.001
Pb	0.005	W	0.005
Mg	0.060	Zn	0.01
Mn	0.005	Co	0.004
Ni	0.007	Ca	0.003
Ti	0.005	Cd	0.00005
V	0.005		

Article by Anon. *Nucleonics* 14, Feb. 1956 45-49

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An Investigation of the Iodide Method of Refining Zirconium — 193/I

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The Dissociation Pressures in the Zirconium—Oxygen System at 1,000°C — 194/I

United Kingdom. A study has been made of the free energy of dissociation in the zirconium-oxygen system at 1,000°C. An alloy of zirconium with 4.8% oxygen was prepared by arc-melting zirconia and zirconium metal. This alloy was equilibrated with excess Mg, Ca or Ba at 1,000°C in a zirconium crucible enclosed in a steel bomb. The product was treated with dilute hydrochloric acid and the zirconium-oxygen alloy powder which remained was washed and dried. Hydrogen was removed from the powder by heating slowly to 800°C in a silica tube connected to a vacuum pump. The composition of the product was determined by chemical, spectrographic and vacuum fusion analysis. The equilibrium concentrations (wt.%) of oxygen found for the three reducing metals was Ca < 0.05: Mgl.55: Ba 2.0. Total reduction of zirconia by calcium and magnesium was also investigated. Use of a $CaCl_2$-flux during calcium reduction gave lower figures for final oxygen, nitrogen, and calcium contents. Magnesium reduction of zirconia gives zirconium contaminated with magnesium. Since in the case of titanium, magnesium may be removed by heating *in vacuo* at ca. 1,400°C, a two-stage reduction of zirconia by Mg and Ca is suggested, with removal of Mg by vacuum evaporation after the first stage. The curve for the free energy of dissociation at 1,000°C for the zirconium-oxygen system has been plotted and compared with the systems of oxygen and titanium, vanadium or iron. The curves show that of the common reducing agents, only calcium may be expected to produce pure titanium or zirconium from the oxides, while vanadium may be produced by magnesium or aluminium as well.

Article by O. Kubaschewski & W. A. Dench *J. Inst. Metals* 23, July 1956 440-444

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Vapour Lubrication of Titanium and Zirconium — 195/I

See Abstract No.: 144/I

What's Wrong with Titanium? — 196/I

United States. A report is given of a symposium on titanium held at the Solar Aircraft Co. plant in Iowa, where sales executives of titanium producing companies and metallurgists from firms utilising titanium discussed critical topics involved in the use of the metal and its alloys. Subjects included testing, storing, forming, heat-treating, welding, coating, and cleaning titanium. Prices and the re-use of scrap titanium were also discussed. The finish and flatness of the material received from the supplier is expected to improve in the future, being at present difficult to attain with higher strength alloys which are difficult to cold roll. Samples of material for testing present a problem. For instance, the analysis for hydrogen of samples from opposite sides of a titanium sheet may give results of 120 p.p.m. on one side and 180 p.p.m. on the other side. Hydrogen content of commercially pure metal is usually below a limit of 150 p.p.m. and is higher at the edges and corners of a sheet. Distribution is uniform throughout bars. It is not likely that the hydrogen content will be reduced much in the near future, and in fact it was doubted whether analysis could show a difference of even 50 p.p.m. with any significance. More reliable methods for aluminium and oxygen analyses are thought desirable, though the Kjeldahl method for nitrogen is satisfactory. The role of hydrogen in causing embrittlement of Ti alloys is not clear. Embrittlement may have other causes in some alloys. In a discussion of physical properties, the effect of the direction of rolling (strip metal) upon properties such as bending, strength and strain rates, was said to be more marked with alloys than with pure Ti. Scratching of titanium is to be avoided in handling. Forming of titanium requires high-power equipment, and is more readily done when hot. This is essential with most of the alloys. Temperatures for forming are 500–600°F for pure titanium, and up to 1,400°F for its alloys. Techniques in welding titanium aim at minimising porosity. Helium, argon, or mixtures of both are used as protective gases. Heat treating at 1,300°F of titanium and alloys after welding or high temperature forming is desirable to stabilise the material to subsequent exposure to high temperatures. A good vacuum, followed by an inert atmosphere, is better for heat treating, than air. The latter necessitates subsequent cleaning. Scale formed below 1,150°F is removed by an acid bath containing nitric acid of a strength above 20–30%. A primary problem in de-scaling is the pick-up of hydrogen, mainly by adsorption. When using hydride solutions for de-scaling, time and temperature must be controlled to minimise pick-up. Preparation of metal surface prior to furnace treatment may facilitate scale removal. Titanium held at 600°F for a long time does not require de-scaling. If titanium is to be annealed by heating above 1,400°F, oil must be previously removed since at this temperature hydrogen pick-up occurs. Coating has been suggested to combat pick-up during heat treatment.

Article by Anon. *Modern Metals* May 1956 68-78

The Melting and Casting of Titanium — 197/I

Germany. The author gives a historical review of the production of titanium, discusses its mechanical and physical properties, describes the Kroll-process and refers to recently developed distillation and melting procedures. 183 References.

Article by W. Scheibe *Giesserei* Jan. 1956 8-17

Chemical Engineering Aspects of Titanium Metal Production — 198/I

United States. The production of titanium, the ninth commonest element in the earth's crust, went up from 50 to 2,000 tons in America between 1950 and 1953. Existing processes for the production of titanium from the ore to sponge titanium depend on the use of titanium tetrachloride which is obtained from rutile ore, which

has a high oxide content, by high-temperature reaction with chlorine in the presence of a reducing agent. At present, the titanium industry is based on the magnesium reduction of titanium tetrachloride (Kroll process). The final step of this process is to separate the metal from the $MgCl_2$ and the magnesium. This can be done by leaching with acid but a recent development is the use of vacuum distillation for this separation. This is carried out at a temperature between 900 and 1,000°C and pressures less than 100 μ Hg. Some practical aspects of maintaining a vacuum on such a system were described in a recent publication by Stoddard and Mooz. Various other methods of reducing titanium from the tetrachloride are under study: One method uses sodium instead of magnesium; fused-salt electrolysis is another. Where extreme purity is desired the iodide process is used. Other methods produce titanium metal of a lower purity, suitable for certain alloys but not for ductile titanium metal.

Article by R. L. Powell *Chem. Engng. Progr.* **50**, Nov. 1954 578-581

199/I

The Powder Metallurgy of Titanium

United Kingdom. Methods of preparing titanium powder are reviewed and the properties and applications of the solid metal produced from it are described. A difficulty in handling titanium is its affinity for gases which dissolve in the metal producing a hardening and embrittling effect. Neither oxygen nor nitrogen can be removed from titanium once they have been absorbed, hence contamination must be avoided at all stages of processing. Titanium powder has been formed by the reduction of titanium tetrachloride vapour with magnesium vapour in an atmosphere of pure argon. Magnesium and magnesium chloride were also formed in the reaction and these were subsequently removed by vacuum distillation or a solution process leaving a fine titanium powder. This was very reactive due to its large surface area and has not yet been used to produce solid parts by powder metallurgy. It may be possible to modify the process to give a coarser, less reactive powder. Titanium hydride powder suitable for pressing and sintering can be made from coarse titanium sponge. The sponge is first heated in vacuum to approximately 800°C to activate its surface and is then cooled to 450°C. Pure hydrogen is introduced into the apparatus and is rapidly absorbed by the titanium. The temperature rise which accompanies this process is controlled by the rate at which hydrogen is added. The sponge is cooled to room temperature under a static pressure of hydrogen and can then be removed and crushed. Alloying elements may be added in the form of pure metal powder or pre-alloyed powder prior to compaction. Hydrogen can be removed from the powder by a vacuum treatment before pressing and sintering but this increases the reactivity of the product and it is preferable to remove the gas during sintering. The removal of hydrogen during sintering has the added advantage that it accelerates the sintering process and gives a higher sintered density. Titanium hydride powder is not so easy to compact as titanium powder and the green densities and strengths obtained are therefore lower. The faster rate of sintering, however, more than outweighs this disadvantage. Sintering becomes rapid at temperatures above 1,000°C. Pressed compacts are almost always sintered in a high vacuum (at least 10^{-4} mm. Hg). Sintering may be carried out in an atmosphere of pure argon but a vacuum is preferred. Relevant data is given in a table, partly reproduced below. Sintering in a molten bath of calcium under an

Shrinkage and Density Measurements for Titanium and Titanium Alloys Prepared Using Titanium Hydride Powder

Alloy	*Sintering Treatment*		*Shrinkage, %*	*Density after Sintering*		*Theoretical Density, g./cc.*
	Temperature, °C	*Time, hr.*		*g./cc.*	*% of theoretical*	
Unalloyed	1200	8	13.2	4.40	97.8	4.50
	1300	8	13.3	4.42	98.4	4.50
10% Cr	1200	8	13.0	4.51	96.7	4.66
	1300	8	13.0	4.52	96.8	4.66
10% Mo	1200	4	12.3	4.49	94.6	4.76
	1200	20	—	4.60	96.7	4.76

inert atmosphere has also been considered. The rate of heating when sintering titanium hydride powder must be slow, particularly in the temperature range 500–800°C when the bulk of the hydrogen present is liberated. It is essential to remove hydrogen completely, otherwise the ductility of the metal is impaired. Pressing and sintering operations can sometimes be combined by hot-pressing the powder. Hot-pressed titanium blanks weighing up to 125 lb. have been prepared using graphite dies in a high vacuum. Powder metallurgy can produce titanium parts with properties comparable to those of metal produced by melting. Pressed compacts are likely to be useful for the large-scale production of small components directly to shape. This would reduce machining and hence scrap losses. Parts could also be forged and machined. Titanium jet-engine bearing housings can be made more cheaply by press-forming sintered powder than by any other method. Powder metallurgy also permits the production of porous bodies and titanium filters might be suitable for applications requiring high corrosion resistance.

Article by D. A. Robins *Light Metals* **19**, Feb. 1956 60-63

200/I

Titanium and Vacuum Heat-Treating Furnaces

See Abstract No.: 113/III

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Titanium Alloy Reclamation by Vacuum Annealing 201/I
See Abstract No.: 115/III

Hydrogen Embrittlement of Commercial Alpha-Beta Titanium Alloy 202/I
See Abstract No.: 116/III

Determination of Hydrogen in Titanium Metal by Hot Extraction 203/I
See Abstract No.: 117/III

Titanium-Carbide-Base Cermets for High-Temperature Service 204/I

United States. Systematic work to produce metal-bonded titanium-carbide parts for high-temperature applications started ten years ago. The development of one specific family of titanium-carbide-base cermets is discussed and their production, properties and applications are presented. These cermets are described as WZ, and fall into two classes. WZ1 materials are titanium carbide with a nickel-chromium binder, and WZ12 have a nickel-cobalt-chromium binder. The binder content may be 25–65%, and the physical properties of the material are dependent on the binder content. A small amount of molybdenum is included to eliminate free carbon and oxygen, which affect the properties. The materials are produced by powder metallurgy methods. High-purity titanium carbide and the alloys are mixed in powder form by ball-milling then cold-pressed, presintered and shaped, and finally sintered in a vacuum furnace at 0.1 mm. Hg. Data on the materials is given in a table, reproduced below. Flexural strength, tensile strength and impact strength increase with binder

Composition and Physical Properties of WZ Alloys

Alloys	*Chemical Composition, per cent*				*Density g. per cu.cm.*	*Vickers Hardness*	*Average Coefficient of Thermal Expansion, per deg Cent, 20 to 1,000C*
	Titanium Carbide	*Nickel*	*Cobalt*	*Chromium*			
WZ-1b	60	32	—	8	6.20	950	10.2×10^{-6}
WZ-1c	50	40	—	10	6.50	790	—
WZ-1d	35	52	—	13	6.90	590	12.6
WZ-12a	75	15	5	5	6.0	1070	9.9
WZ-12b	60	24	8	8	6.25	960	9.2
WZ-12c	50	30	10	10	6.55	820	10.6
WZ-12d	35	39	13	13	6.95	600	11.9

content, while modules of elasticity and stress-to-rupture strength decrease with increasing temperature, especially for the higher binder content materials. Impact strength increases somewhat at 900°C compared with room temperature. Stress-to-rupture strength values also decrease at higher temperatures with increasing binder content. Oxidation resistance at 1,000°C is improved by a high proportion of binder, a protective oxide layer being formed. Resistance to heat shock has been tested by repeated quenchings in cold air from 1,800–2,400°F. Most WZ alloys withstand this test without cracks occurring. Analytical methods include magnetic methods and Zyglo porosity. WZ wheels have shown excellent properties in hot spinning tests, and methods for the production of turbine buckets, nozzle deflection vanes, valves, furnace gear etc. are being developed.

Paper by K. Pfaffinger, H. Blumenthal & F. W. Glaser *Symposium on Metallic Materials Above 1600°F A.S.T.M.* 1955

Good Control Makes Titanium Welding a Shop Tool 205/I
See Abstract No.: 92/I

Gettering of Gas by Titanium 206/I
See Abstract No.: 10/I

Molybdenum 207/I

United Kingdom. Commercial and technical information is given on the production, fabrication and application of molybdenum. The chief source of the metal is molybdenite and the largest mine of this mineral is operated by the Climax Molybdenum Co. in Colorado. Some copper and tungsten mines produce molybdenite as a by-product and a little metal is obtained from the ore Powellite. In 1953 the United States contributed about 92% and Chile about 5% to the total production of molybdenum concentrates. Other producing countries

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include Canada, Japan, Korea and Australia. The estimated ore reserves of molybdenum in the U.S. are equivalent to 100 years supply at the wartime rate of use. In producing the metal the molybdenite is first converted to oxide by roasting in a free flow of air. The oxide is purified and then reduced in a stream of hydrogen. Water vapour produced in the reaction is carried away leaving a metal powder which can be compacted either by pressing and sintering or by arc-melting. Arc-melting is the more suitable method for large billets, and arc-melted ingots weighing up to 1,000 lb. have been produced by the Climax Molybdenum Co. This method is being studied in England by the Ministry of Supply Armament Research Establishment at Woolwich. The largest U.K. producer of molybdenum is Murex. Molybdenum is a comparatively ductile metal and can be worked to most of the forms required by industry. It is difficult to weld, however. Sheet 0.04 inch, 0.02 inch, and 0.01 inch thick, made from pressed and sintered metal is sold in the U.K. for £8.10.0, £10.1.0. and £13.2.6 per kilo respectively. Prices quoted by the Climax Molybdenum Co. for arc-melted metal are as follows:

Material	*Per lb. f.o.b. Detroit*
	Dollars
Turned ingots approximately 6½ inch. dia. × 22 inch. long	5.85
Turned extrusions approximately 3¾ inch. rd. (from under 50 lb. to over 2,500)	10.05– 8.00
Sheet bars approximately 1 inch × 3¾ inch. (for re-rolling) (from under 50 lb. to over 2,500)	12.05–10.00

In the U.S. in 1952 about 91.5% of the molybdenum consumed was used in the iron and steel industry and about 1.9% in the manufacture of molybdenum metal. Molybdenum is also used in paint, welding electrodes, catalysts and lubricants. The chief advantages of molybdenum used as a metal in its own right are its high strength and rigidity at elevated temperatures. It is used in electrical, electronic and high-temperature applications: For example, in incandescent and fluorescent lamps, electric furnace resistors and electrical contacts. The thermal-neutron absorption characteristics of the metal make it suitable for use in reactors, particularly for those operating at temperatures above 870°C. Further advantages of the metal are its low expansivity, high thermal conductivity and resistance to liquid sodium and lithium which may be used as coolants in high temperature reactors. The good high-temperature properties of molybdenum and its alloys have led to considerable development work on their application in gas engines, ram jets and guided missiles. A disadvantage, in this field, is the poor resistance of the metal to oxidation. Attempts have been made to protect molybdenum by metal coatings and it has been found possible to provide sprayed coatings with a minimum life of 500 hours plus at 1,000°C and of 100 hours plus at 1,100°C. Successful protection from oxidation of molybdenum alloy blades and guide vanes would permit an increase of 50% or more in output from the gas turbine by increasing operating temperatures by about 150–200°C. The adjustment of the combustion gases to avoid the presence of oxygen is being investigated as a means of safeguarding unprotected molybdenum components.

Article by G. L. Miller *Times Rev. Industr.* May 1956 28, 31

208/I

The Present State of Molybdenum Production

Austria. Methods of producing molybdenum ingots, in particular the high-vacuum arc casting process used by the Metallwerk Plansee, G.m.b.H., Reutte are described. The direct sintering, or Coolidge process, in which compact metal powders are sintered by direct passage of electric current, gives a very pure, gas-free, deformable metal, but the maximum weight of the ingots is limited to about 10–15 kg. Larger ingots weighing 15–100 kg. and shaped pieces can be obtained by the indirect sintering process in which the compacts are sintered in a furnace, usually a muffle furnace with a hydrogen atmosphere. The high operating temperatures require the use of molybdenum or tungsten heating elements and special alumina refractories. A slightly porous, not too large-grained metal structure is obtained which is suitable for further processing. The high-vacuum arc casting method used by the Metallwerk Plansee is based on the process developed by the Climax Molybdenum Co. but differs in that the electrode is prepared in a separate processing step outside the melting apparatus. This electrode consists of high-sintered molybdenum bars joined, mechanically or by arc-welding, to a long electrode rod and placed in a tube on top of the furnace. The movement of the electrode is controlled by a mechanism which governs the arc and keeps the arc voltage constant. The crucible consists of a water-cooled copper tube constructed to permit continuous lowering of the crucible bottom. The furnace chamber is connected directly with an oil diffusion pump having a capacity of 8,000 litres per second at 10^{-4} mm. Hg. A rotary pump provides the fore vacuum. Deoxidation is preferably effected by adding fixed amounts of carbon to the starting powder. The carbide precipitates are globular and have far less effect on deformability than the oxide found at the grain boundaries of non-deoxidised material. Cast metal contains less oxygen but more carbon than sintered molybdenum and other impurities are about the same. Large dense ingots are obtained. Rough and porous surface layers are removed by a preliminary turning operation and the ingots are then rolled and forged at high temperatures. A method found suitable for the initial working of cast ingots is glass-skin extrusion by the Ugine-Séjournet process in which, after a single heating step in a salt bath or protective atmosphere, the material is forced rapidly through a nozzle by high-capacity extrusion equipment. The extruded metal can be processed to sheet, bar and wire using equipment as developed for stainless steel. An advantage of arc casting, as compared with sintering, is that larger semi-finished units can be obtained. Cast molybdenum is easier to machine and deform and has better welding properties. Alloying additions in powder form may be pressed into the

electrode, although for a fully homogenised alloy a second casting operation is necessary. Scrap losses are lower since up to 30% of comminuted chips can be pressed into the electrode. Molybdenum is characterised by a high melting point, *i.e.*, 2,600°C, and low vapour pressure and good electrical properties even at high temperatures. It has good corrosion resistance and high hot-strength. The impurity content of cast and sintered molybdenum is given in a table, reproduced below.

Impurities	*Cast Molybdenum*	*Sintered Molybdenum*
Oxygen	0.0002–0.002 average 0.0007	0.0005–0.007
Nitrogen	0.0001–0.0002 average 0.00011	0.0001–0.004
Hydrogen	0.0001–0.0002	0.0001–0.0003
Carbon	0.02 –0.04	0.002 –0.003

Article by R. Kieffer & F. Benesovsky *Powder Metal Bull.* 7, April 1956 113-121

A Metallurgical Study of Molybdenum

209/I

United States. A final report is given of the research project on molybdenum sponsored by the Office of Naval Research and carried out at Battelle from 1949 to 1954. Most of the work was concerned with improving the room temperature ductility of molybdenum. It was found that impurities, particularly oxygen and carbon, precipitated at grain boundaries were the prime cause of brittleness. The critical amount of the impurities was so small that special analytical methods were required to investigate them. A vacuum fusion apparatus was developed which could measure oxygen with a sensitivity of $\pm 0.0001\%$ provided large samples (10g) with a low ratio of surface area to volume were used. Nitrogen was analysed by a modified vacuum fusion technique described as a diffusion-extraction method. In this method, which gives a sensitivity of 0.00005%, the usual iron bath was eliminated since it was found to retain some of the nitrogen. Improved techniques were also developed for analysing carbon, sulphur and metallic elements. Studies on the solubility of impurities in molybdenum were carried out in a resistance furnace under an atmosphere of argon, hydrogen or low-pressure oxygen. Before the precise effect of specific impurities could be determined it was necessary to obtain pure molybdenum which could subsequently be contaminated by known amounts of 'impurities'. One method of refining was by vacuum fusion purification in which the metal was arc-melted several times under vacuum. A water-cooled molybdenum-tipped electrode was used to melt sintered bars under a pressure of less than 0.1 μ. Melting three times (two remelts) gave the lowest impurity content. Thin sections were successfully refined by 'solid state purification' which consisted of prolonged heating in vacuum at temperatures above 3,500°F but below the melting point of molybdenum. This method was not suitable for thick sections since they required long heating times during which carbon was picked up from the furnace atmosphere, possibly because of the presence of oil vapour. The room-temperature ductility of pure molybdenum was much greater than that of commercial metal. The ductility of the solid-state-purified metal was influenced by the rate of heating to the treating temperature, and possible explanations of this phenomenon are examined. Molybdenum was found to be extremely sensitive to oxygen and in some cases an increase in oxygen content from 0.0001% to 0.0002% resulted in a change from ductile to brittle behaviour. Even when present only in solid solution carbon decreased the ductility of the metal. Sulphur itself had no effect on ductility but some impurity present in commercially purified sulphur is of importance. Nitrogen had an embrittling effect but was not usually present in sufficient amount to cause trouble. Various elements were added to melts in efforts to neutralise harmful impurities and, of these, titanium proved the most effective in improving room temperature ductility. In research on the welding of molybdenum ductile welds were only obtained with resistance butt welds made in a high vacuum between ¼-inch. high-purity rods using a metallographic polish and an electrolytic etch on the surfaces. No ductile welds were obtained in an inert atmosphere and experiments in various air pressures indicate that for successful welding an inert gas would have to be very pure. Work on the development of oxidation-resistant alloys of molybdenum proved unsuccessful. A chapter on possible lines of future research indicates the need for further work on the plasticity of molybdenum and the quantitative effects of impurity elements. The latter would require an improvement of the Kjeldahl analysis of nitrogen and improved means of measuring sulphur, for example by a vacuum-fusion method. It would be useful to analyse solid-state purified molybdenum without exposure to air between purification treatment and analysis, in order to investigate the effect of surface oxidation and adsorption. Further work is necessary on the use of alloying additions or heat treatment to neutralise effects of impurities. Processing methods and protection against oxidation also require development.

Report by S. L. Case *Battelle Memorial Inst. Rep.* PB 111753 15.10.54 74 pp.

Rhenium

210/I

United Kingdom. Attention has recently been focused on the metal rhenium, which may become available soon in commercial quantities in the United States. The results of an investigation of its physical and mechanical properties, made by the Battelle Memorial Institute, are reported. Rhenium powder was produced by hydrogen reduction of ammonium perrhennate. Sintered bars were made by pressing rhenium powder (1–25 micron) at 30 tons per sq.inch., pre-sintering in a vacuum at 1,200°C, and then sintering in hydrogen at 2,700°C, the bars being resistance-heated by a current of about 1,200 A. Rhenium could also be formed by deposition from a rhenium halide on to a hot tungsten wire. Either form could be converted into buttons by arc-melting under argon. None of the forms could be successfully hot-worked. Cold working was partially successful with arc-cast material, but not with hot-wire deposited rhenium. Sintered rhenium bars could be fabricated into rods, wire, sheet and foil by cold-working and annealing. Rhenium is outstanding for its high work-hardening

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capacity. When it is reduced 30% by swaging, its hardness increases from 250 to over 800. A temperature of over 1,700°C is required to soften it to below 300 for further cold-working. Rhenium is stable in cold air, but oxidises rapidly when heated. A number of physical properties have been determined, including melting point—3,180±20°C, density 21.02, electrical resistivity (20°C) 19.14 microhm-cm. coefficient of expansion (20–1,000°C) 6.8×10^{-6} per deg. C. The electrical resistivity increases with increased cold work. Tensile tests on annealed rhenium at room temperature showed a large spread between yield and ultimate strength. A reduction of 15%, by cold work of annealed rhenium raised the tensile strength from 73 to 150 tons per sq.inch. Elevated temperatures reduce the strength, so that at 1,500°C cold-worked rhenium has nearly the same strength as annealed metal. The effect is much more marked than with tungsten or wrought molybdenum. It is possible that a fine, fully drawn rhenium wire might have a greater tensile strength than one of tungsten. Apart from wear-resisting applications of rhenium and its alloys, it has a number of potential commercial uses in electron tube filaments, cathodic emitters or as an electrical contact material.

Article by Anon. *Engineer* 199, 1.4.1955 452-453

211/I

Spectral Emmissivity of Rhenium

See Abstract No.: 113/I

212/I

Columbium's Chequered History

United Kingdom. This element was discovered in 1801 by Charles Hatchett, who found it in a specimen of the mineral columbite in the British Museum. The German chemist Heinrich Rose, in 1844, investigating a similar mineral, found that a second element was present with the tantalum in it and named this niobium. Though the formula for columbite is given as (FeMn) $0.(CbTa)_2O_4$, the mineral is called tantalite or columbite depending on tantalum or columbium being in excess. After these confused beginnings, interest centred on obtaining the pure metal. An impure specimen was prepared by C. W. Bloomfield in 1864 and in 1901 Henri Moissan produced a small ingot of columbium which, however, was not free of carbon. It proved so inert and refractory that he imagined it might be non-metallic. In 1906, Werner von Bolton reduced columbium oxide with aluminium powder to form the metal. He was looking for new materials for incandescent lamp filaments and had already made tantalum filaments by a method akin to powder metallurgy. Columbium dissolves slowly in *aqua regia*, behaving in a manner intermediate between platinum and tantalum. It does not become brittle, as does tantalum, on heating and has a resistance towards atmospheric corrosion intermediate between tantalum and tungsten. Columbium may find an application in high vacuum electronic tubes, as it has 'getter' properties superior to tantalum. The carbide of columbium is invaluable in machine tools and for wire drawing. Additions of up to 1% of the metal are used in stainless austenitic steels to prevent 'weld decay'. The metal is available as sheet, wire, rod and tube, and aluminium-columbium alloys have been marketed. Applications of it, however, are handicapped by its rarity and cost.

Article by M. Schofield *Discovery* 17, Feb. 1956 75

213/I

The Structure and Growth of Oxide Layers Formed on Beryllium

See Abstract No.: 58/III

214/I

Mechanically Sealed Beryllium Windows for Permanently Evacuated X-Ray Tubes

See Abstract No.: 102/II

215/I

The Sintering, Fabrication, and Properties of Thorium

United Kingdom. Because of the great difficulty in melting thorium, since it is extremely reactive, most work has been in the field of powder metallurgy. This investigation is concerned with a study of the efforts of a range of compacting pressures and sintering temperatures. The sintering was carried out in a platinum-wound furnace at a pressure of about 4×10^{-5} mm. Hg. The optimum results as judged by density and resistivity determination were found to be obtained by pressing at 22.5 tons/inch.^{2} and then sintering for 2 hr. at 1,300°C. Metal of density approaching the theoretical was obtained by re-sintering after cold rolling to 50% reduction of thickness. Re-sintered metal, although of an average oxide content of 1.75 wt.-%, was still very ductile. The influence of cold rolling on the mechanical properties of thorium has been determined and the recovery and recrystallisation of the cold-worked metal on subsequent annealing has been investigated for a range of deformations and temperatures.

Article by M. D. Smith & R. W. K. Honeycombe *J. Inst. Metals* 22, May 1955 421-426

216/I

The Routine Determination of the Hydrogen Content of Aluminium and Aluminium Alloys by the Hot-Extraction Method

See Abstract No.: 118/III

217/I

The Electrical Resistance of Pure Vacuum-Sintered Aluminium Oxides

Germany. The resistance of Al_2O_3 is known to depend on the temperature and, although this property has been investigated in the past, usually no reliable information was available on purity of the material used or the method of its preparation. Knowledge of all chemical and physical factors which govern the electrical resistance of the ceramic oxides, is essential for the correct prediction of changes in resistance, etc. The authors

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measured the resistance *vs.* temperature of Al_2O_3 samples of great purity, prepared by themselves. The starting material was pure aluminium which was transformed into α–Al_2O_3 by heating. Details of the method of preparation are given. Impurities could be assumed not to exceed 0.03%. The Na content varied from 0.015 to 0.025%. The Al_2O_3 powder was then wetted, pressed into a small rod, and pre-sintered for about 5 hours in a tubular furnace at 1,000°C. The final sintering and subsequent measurements took place in high vacuum. During sintering, the high vacuum was about 10^{-5} mm. Hg and care was taken to prevent back-streaming. Sintering time was 30 minutes at a temperature of 1,800°C. For the measurements platinum electrodes were clamped on to both ends of the Al_2O_3 rod which also held the rod suspended inside an Al_2O_3 tube. The Al_2O_3 tube carried windings of molybdenum wire and acted as heating device for the temperature resistance measurements. The whole assembly was surrounded by an evacuated bell-jar. The temperature could be raised to 1,500°C and was measured with a thermocouple. The test-results were compared with figures obtainable from investigations on commercially available Al_2O_3. At high temperatures the curves are identical. At lower temperatures the purer Al_2O_3 has the higher resistance ($10^{14}\Omega$). The curve follows the expression:

$$\sigma = a \times e^{-E/KT}$$

Article by K. Heldt & G. Haase *Z. Angew. Phys.* 6, No. 4. 1954 157-160

The Preparation and Properties of High-Purity Iron 218/I

United Kingdom. Methods for producing high-purity iron are mainly chemical or metallurgical, electrochemical methods not being favoured because of their low degree of purification. They involve the purification of iron compounds and metallic iron respectively, and their selection must be governed by considerations of the amounts and degree of purification required and of the available starting materials. Of chemical methods, the ferrous oxalate, ferrous formate, and ferrous sulphate methods were not promising largely because of the persistence of metallic impurities, particularly manganese. A method employing cupferron (ammonium *N*-nitrosophenyl-hydroxylamine) was difficult and expensive. Investigation by Cleaves and Thompson of the ferric nitrate method showed that the manganese was reduced beyond spectrographic detection and that other impurities were removed to a greater extent than by other methods. Electrolytic iron as starting material was converted to ferric nitrate, recrystallised six times by nitric acid, and converted to ferric oxide, by means of ammonia. Details of the results are given in tabular form. Adcock dissolved electrolytic iron in high-purity hydrochloric acid, crystallised the ferrous chloride, converted it into oxide with a steam-air mixture at 250°, and reduced the oxide by hydrogen to iron powder, following this by sintering and melting. The process reduced the contents of phosphorus, copper and nickel, and removed silicon. Moore investigated ferric chloride methods, in which the basic step was purification of the ferric chloride by ether extraction. The process stages were ether extraction of $FeCl_3$ complex from solution in 6 *N*-hydrochloric acid, reduction of $FeCl_3$ to $FeCl_2$ with high-purity iron, additional purification of $FeCl_2$ by recrystallisation, sulphide precipitation, or ether extraction of impurities from ether-insoluble $FeCl_2$ solutions and electro-deposition of iron from $FeCl_2$ solution. Metallurgical methods of purifying iron can be carried out with the iron in the liquid or solid state. In the latter, moist and then dry hydrogen is used to reduce the carbon, oxygen, nitrogen, and sulphur contents. Two methods involving melting, *i.e.* the Fast, and the Hopkins, Jenkins and Stone method require operation *in vacuo*. A review is given of the various methods with a description of the equipment. Data are given of the more important physical properties of high-purity iron, including density, freezing point, boiling point, A_3 transformation, A_4 transformation, lattice parameters, coefficient of expansion, thermal conductivity, specific heat, thermal electromotive force, electrical resistivity, and magnetic properties. In a discussion of mechanical properties (tensile, notched-bar impact, hardness and modules of elasticity), attention is paid to polycrystalline iron, single crystals, and the crystallography of slip in iron single crystals.

Article by B. E. Hopkins *Metall. Rev.* 1, Part. 1 1956 117-155

Vacuum-Melted Antifriction Bearing Steels 219/I

See Abstract No.: 99/III

The Bochumer Verein Vacuum Casting Process 220/I

See Abstract No.: 45/I

Method of Preparing Metal and Apparatus Therefor 221/I

See Abstract No.: 108/III

Sublimation Figures in Nickel, Copper and Zinc 222/I

United States. Regular patterns have been observed on the surfaces of vacuum-melted metals from which sublimation has taken place. A cubic figure for instance, was found on pure nickel specimens used in vacuum evaporation experiments. Investigating the matter further, specimens of zinc, copper and iron were prepared in the form of 40 g. buttons and were melted under a residual pressure of less than 5×10^{-4} mm. Hg. After solidification, the specimens were held for a short time at a temperature slightly below the melting point to permit sublimation, cooled in the vacuum to room temperature and then examined under the microscope without further preparation. Hexagonal figures were observed on the zinc and circular figures on the copper specimen. Sublimation patterns were not found on the iron, but it is likely that the solid state transformations

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I — General Science and Engineering — I
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which occur in iron would destroy any surface figures originally present after solidification. The development of a well-defined figure within a single grain implies a mechanism of sublimation comparable to the spiral growth process of crystallisation from dilute vapours. In a certain range of temperature the rate of sublimation may be such that atoms are removed from the metal surface in an orderly manner. An atom exposed on three faces is the easist to remove. Its departure exposes a second atom and the process is repeated until inhibited by some inhomogeneity in the crystal. This process is similar, in reverse, to that calculated by Burton, Cabrera and Frank for crystal growth. It indicates that screw dislocations may permit sublimation at temperatures at which the vapour pressure corresponds to low supersaturations. The stepped surface resulting from such a process could not be resolved under the optical microscope. It is possible, however, that slip resulting from contraction of the specimens on cooling may develop the steps of the sublimation figures to such an extent that they can be observed.

Article by J. C. Danko & A. J. Griest *J. Metals Trans. AIME* 8, May 1956 515-516

223/I **New Isotope Separation Process Pushed in Germany**

See Abstract No.: 10/IV

224/I **Applications of Radioactive Materials to the Problem of Metals of Very High Purity**

France. The use of radioactive materials in the study of metals of extremely high purity has proved very useful because of the great sensitivity of these methods with respect to the traces of impurities still present in such metals. The author describes some typical methods developed by himself at the Centre d'Etudes de Chimie Metallurgique (Vitry) and based on the use of radio-active materials. In addition, tracer techniques facilitate the study of the mechanism responsible for the elimination of impurities. By way of example, studies of the decarburisation of iron by means of annealing in pure hydrogen are mentioned. Finally, reference is made to tracer techniques, employed for the determination of the distribution of the minute impurities in the purified metal.

Article by P. Albert *Chim. & Industr.* 75, Feb. 1956 275-286

225/I **A Furnace for Obtaining Optical Spectra of Radioactive Elements**

United Kingdom. A furnace, such as that used by King for emission and similar to that used by Paul, Bovey and Garton for absorption spectra, has been designed for use in obtaining the emission and absorption spectra of radioactive or toxic materials such as uranium and plutonium. The furnace element is a graphite tube 6 inch. long heated to about 2,500°C. This cylinder is mounted between graphite and plates which carry cylindrical graphite radiation shields co-axial with the furnace tube. For added radiation shielding, tantalum sheets, spot welded into cylinders of the same diameter, were mounted on the graphite. Two further discs of tantalum were mounted either end of the furnace tube and the whole assembly enclosed by a vacuum-tight, water-cooled, mild steel cylinder. Quartz windows at either end permitted light to pass axially through the furnace for observation of the spectra. A demountable flange at one end of the cylinder was mounted on rails so that the graphite cylinders, which were fixed to it by the water-cooled copper tubes acting as current leads, could be removed for easy replacement of the furnace elements. A sintered, seamless tantalum liner $\frac{1}{2}$-inch. in diameter and 0.02-inch thick was used in the furnace tube, as it had been found by Bovey and Barton that uranium attached the graphite element. The whole apparatus was enclosed in a transparent 'dry' box to confine the material handled. Manipulations inside the box were carried out through standard rubber gloves assemblies let into the side. The furnace was evacuated during use. The elements were heated under vacuum to outgas them and allowed to cool before the material was introduced. A second evacuation was then effected before the furnace was sealed from the pump and heated. The absorption spectra of scandium, yttrium and lanthanum together with the absorption and emission spectra of uranium and plutonium were taken during preliminary runs with the furnace. These are now being examined and the results will be reported later.

Article by L. F. H. Bovey *J. Sci. Instrum.* 32, Oct. 1955 376-378

226/I **High-Temperature Vacuum Furnace for Tensile Testing**

See Abstract No.: 153/III

227/I **Technical Aspects of Levitation**

See Abstract No.: 145/I

II — Vacuum Apparatus and Auxiliaries — II

Abstract No. and References

20 — PUMPS — 20

Vacuum Technique 1/II

See Abstract No.: 2/I

Mechanical Vacuum Pumps 2/II

Germany. The author reviews recent design development in the field of mechanical vacuum pumps. Particular reference is made to the operational and economical conditions with respect to gas ballast pumps and certain types of the same fitted with automatic oil decontamination equipment. Pumping combinations using the Roots pump as the high vacuum pump are also discussed and are particularly useful for large throughputs in the region above 100 m^3./hour.

Article by H. Bürger *Chem. Technik* 8, April 1956 218-232

Improvements i.o.r.t. Rotary Vacuum Pumps 3/II

United States. In rotary vacuum pumps of the two-stage type the rotors of the two stages are normally mounted on a common shaft in a single cast housing, and the centre wall which separates them is machined on both sides. The machining operation removes the surface skin from the cast faces, and it is often found that the metal thus exposed is sufficiently porous to lead to appreciable inter-stage leakage. In this design the centre wall is replaced by a partition, left hollow by coring during casting, so that at least one unbroken skin is maintained between its machined faces. This skin is practically impervious to the vapours pumped. The hollow so formed is divided into two chambers by a web, which has at its centre a hub carrying the shaft bearing. The hub is the only part of the partition not having an unbroken skin, but is long enough axially to prevent leakage. One of the chambers is made to serve as the inter-stage transfer duct and also as the first stage oil reservoir, from which oil is distributed through suitable channels to both the centre bearing and to the moving parts of the first stage. This position of the shaft bearing enables the bearing, usually provided in the outer end cover of the first stage, to be dispensed with.

H. G. Bowering & New York Air Brake Co. *Brit. Pat.* 739-824

Improvements in Rotary Pumps or Compressors 4/II

United Kingdom. A novel design of rotary pump is described which aims (*a*) at reducing wear and tear produced between the blades on one hand and the rotor on the other, and (*b*) at reducing the noise caused by vibration. The new design provides for each of the two blades to be of a depth greater than the maximum diameter of the rotor and to be positioned in the conventional rotor slot on top of each other in such a manner, that the apertures provided in the central portion of each blade overlap and that springs accommodated in these apertures exercise the necessary thrust in the required opposite directions for the blades to make and keep contact with the stator surface. In addition, the surface of the stator casing is formed with a profile comprising two circular arcs of the same radius centred at points situated symmetrically on opposite sides of the diameter of the rotor passing through the location of engagement of the rotor with the stator surface, which arcs are joined by two circular arcs of the same radius centred on the diameter in question.

Metropolitan-Vickers Electrical Co. Ltd. *Brit. Pat.* 739-334

Four Problems Regarding the Amount of Air Displaced by a Compressor or a Rotary Pump 5/II

Rumania. An expression for the air displaced by a compressor or rotary pump is developed and the influence of the thickness of the vanes, their angular position and the size of the compressed angle on the displacements has been investigated.

(*Author*)

Article by C. Buda *Bull. Inst. Polit.* No.1-2, 1955 325-335

Vapour Pumping Characteristics of Gas Ballast Pumps 6/II

See Abstract No.: 4/I

Improvements i.o.r.t. High-Vacuum Pump Systems 7/II

United Kingdom. In two-stage rotary vacuum pump systems employing a sealing fluid, such as oil, the latter frequently becomes contaminated with substances of a high vapour pressure, causing liquefaction of the contaminants and consequent reduction in pumping efficiency. The impurites may be removed from the oil by interposing a separator tank of conventional design between the two stages and fractionating the contaminants by evaporation. The fluid is circulated through the separator by means of a pump fitted with a non-return spring-loaded valve.

H. Smethurst & General Engineering Co. (Radcliffe) Ltd. *Brit. Pat.* 754,963

Improvements r.t. Vacuum Pumps 8/II

United Kingdom. An adaptor is described which can be fitted to the outlet of a rotary pump, operating in air, so as to direct the exhaust stream of gas to flow over the body of the pump. The device is to serve as a silencer, and essentially consists of a pipe screwed into the exhaust outlet and leading to a hood, closed at one end concentric with the pipe and having a series of outlets round the end nearest the pump body, These outlets direct the stream of exhaust gas so as to produce a cooling effect on the pump.

T. L. Clark & Alfa-Laval Co. Ltd. *Brit. Pat.* 754,333

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9/II

B. D. Power & W. Edwards & Co. (London) Ltd. *Brit. Pat.* 757,920

Improvements i.o.r.t. Vacuum Pumps

United Kingdom. A safety device is described which will operate if the flow of gas through a pumping system exceeds that occurring in normal operation. The novelty lies in putting the device in the outlet from the backing pump, where the pressure is highest thus facilitating the use of a more robust instrument. The invention proposes that a throttle or constriction should be placed in the outlet pipe, so that a leak, for instance, will cause a considerable build-up of pressure across the constriction, which may be used to operate an alarm, etc. The construction adopted shows the normal pump outlet tube is closed by a spring-loaded valve, and an alternative outlet provided through a capillary tube. The space between the pump and the capillary also communicates with a pressure chamber closed by a flexible diaphragm. When an excessive amount of air passes through the pump, the pressure at the outlet rises and the diaphragm flexes, operating a microswitch, which may sound an alarm, switch off the pump motor, etc. During the initial rough pumping, the switching circuit is disconnected and while the gas flow is very large, the spring loaded valve opens and allows an easier passage to the gas. Later, the valve closes and the normal gas flow passes easily through the capillary. The switch can be prevented from operating on transient increases in gas flow (*e.g.* due to outgassing) by having a pressure chamber of sufficient volume. An example is quoted of a rotary pump having a speed of 50 l./min. backing a diffusion pump having a speed of 50 l./sec. Leakage sufficient to cause a pressure rise of only 5×10^{-3} mm. on the fine side of the diffusion pump and of 0.3 mm. on the fine side of the rotary pump, gave a rise of 10 mm. above atmosphere in the pressure chamber of the device—sufficient to operate the microswitch.

10/II

Article by R. Thees *Vacuum* 5, October 1955 25-34

Roots Pumps Design and Performance Features

Germany. Roots pumps have been specially designed for use with processes which require ultimate pressures in the intermediate vacuum range, the millimetre range. The working principle of the Roots pump is discussed and major points of interest in connection with its application are examined. The limitations of the Roots principle are essentially its restricted compressibility and the generation of heat in the compression stage. Details are given of measures taken to widen the range of pressures where the Roots pump is a practical and economical proposition.

11/II

E. Leybold's Nachfolger *German Pat. Appl.* L. 19097 Ia/27d

Pumping Aggregate for High Vacuum Systems

Germany. Reference is made to the German Patent 884,851 which describes a pumping aggregate, consisting of fore vacuum pump, intermediary pump (if required) and high vacuum diffusion pump, which does not require mechanical valves for its operation. Instead, the pipe line connecting the fine side of the fore pump directly with the recipient to be pumped and the line (if any) connecting the intermediary pump with the recipient are of dimensions which will restrict the back diffusion of gas from these stages into the recipient to an amount considerably lower than that which the high vacuum pump can cope with. In the present Patent Application it is proposed to employ a pump of high volumetric capacity but low compression ratio as the intermediary or (high) vacuum pump, such as the Roots blower, which has proved particularly suitable for this purpose.

12/II

Article by C. S. M. Perez A. L. Sainz *Ion* 15, Oct. 1955 539-545

Units for the Production of High Vacuum

Spain. The article describes the working characteristics of two pumping units, each consisting of an oil diffusion and a mechanical pump. Graphs are shown for the pumping speed and the factors that influence the speed, such as the heating load installed in the diffusion pump, fore vacuum pressure and refrigeration. Data is also given on the pumping times required to reach the ultimate vacuum depending on the heating load. All plant used in the experiment described was manufactured by the Instituto Leonardo Torres Quevedo.

(*Authors*)

13/II

Siemens-Schuckertwerke A. G. *Brit. Pat.* 746,365

Improvements i.o.r.t. a High Vacuum Pumping Device

Germany. A high vacuum pumping arrangement is proposed which essentially consists of an oil diffusion pump working into a mercury vapour jet pump which in turn is working into an oil sealed rotary pump. The intermediary mercury vapour jet pump is to replace the oil booster pump. By using a mercury pump, the latter may be smaller and the rotary pump could be replaced by an oil jet pump as the demands on the fore vacuum are considerably reduced. A heating device is connected to the input and the output side respectively of the intermediary mercury vapour jet pump, in order to decompose oil vapours, which may reach that pump from either side, and convert them into permanent gases which are substantially harmless to the operation of the mercury vapour jet pump.

14/II

Article by H. G. Nöller *Vacuum* 5, Oct. 1955 59-76

The Physics of Modern Vapour Pumps with Particular Reference to Diffusion Pumps

Germany. The physics of the working principle of the vapour pump are discussed in the light of present-day knowledge. Firstly, the conditions obtaining in the beam of the vaporised pump fluid are examined with particular reference to the compression mechanism of the fore vacuum area. Secondly, a study is made of the diffusion mechanism of the gas pumped, in particular its ability to penetrate the vapour beam and the factors which govern pumping speed. There follows a discussion of the operational conditions in the diffusion and jet pump, giving at the same time an indication of their relative ranges of application. Finally, special aspects related to the use of oil in diffusion pumps are treated at length, in particular the problem of ultimate pressures and backstreaming. The article concludes with some remarks on the future prospects of the diffusion pump.

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Improvements i.o.r.t. Vapour Vacuum Pumps

15/II

United Kingdom. A means is described of reducing the loss of fluid from a diffusion pump when handling a large throughput of gas. Under these conditions, which may arise if a leak develops or if a system is pumped from atmospheric pressure without a by-pass line for rough pumping, a considerable quantity of the working fluid may be carried away as a very fine mist, difficult to remove by conventional scrubbers. The invention described operates by breaking up the mist-laden air stream into smaller streams which are accelerated and directed against an obstacle so as to cause a sharp change in direction. The air molecules change direction, but the heavier drops of fluid strike the obstacle and so are removed from the air stream. Three forms of the device are described; each is used in the outlet of the pump. In one, the air stream first passes through a disc pierced with a number of holes to give the acceleration. Immediately behind this plate is another, also perforated, but arranged so that the holes in the second are not in line with the holes in the first. Two such pairs of discs are shown, followed by a pair of more finely perforated plates which may be made from wire gauze, to remove any large droplets which may remain. In the second form, for use where the outlet tube is vertical, pairs of cylindrical cups, perforated in their curved surfaces, replace the discs. With either form, the size of the accelerating apertures has to be calculated knowing the rate of flow of the gas stream, and so different sets of plates or cups would have to be used to suit different backing pumps. The third form of the invention shows a plate with a single slit of adjustable width, followed by an obstacle in the form of a strip overlapping the slit. Tests in which a volume of 3 l. was pumped from atmospheric pressure through a hot vapour pump showed a 5:1 improvement in the rate of loss of pump fluid. In all cases, means are provided to allow the fluid recovered to drain back into the boiler.

A. S. D. Barrett, B. D. Power & W. Edwards & Co. (London) Ltd. *Brit. Pat.* 748,376

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Diffusion Pumps with Freon-12

16/II

See Abstract No.: 6/I

Booster and Molecular Air Pumps

17/II

See Abstract No.: 5/I

Theory of Molecular Pumps Operating at Low Pressures

18/II

France. Integral equations for the pressure distribution in molecular pumps are developed, based on operational conditions generally but taking into account outgassing from the pump walls. The values obtained from these expressions for the case of rotor and stator being concentric cylinders are compared with values obtained by practical experiment and are found to be in general agreement.

Article by C. Mercier *J. Phys. Radium Suppl.* 17, March 1956 1A-11A

High-Vacuum Molecular Pump

19/II

Holland. Molecular high vacuum pumps are often constructed in two main parts: A rotor, and a stator which closely surrounds it. In either the rotor or the stator a shallow helical groove is normally provided, which decreases in cross-sectional area from the low to the high pressure end of the pump, resulting in many machining difficulties. In the arrangement described the rotor and stator are made with a frusto-conical shape. The groove can therefore be machined to a constant depth from the axis of rotation, since the inclination of the surface to the axis now produces the necessary change in groove area. The rotor is also spring loaded axially so that an excessive pressure on the high vacuum side causes the rotor to withdraw slightly from the stator until the pressures are equalised. A further feature is the provision of a hollow rotor having a second stator inside it and a second groove in parallel with the first, so that the pumping capacity is doubled for very little increase in size. This principle may be extended to a multiple system of co-axial rotors and stators.

A. C. van Dorsten A. Verhoeff & Hartford National Bank & Trust Co. *U.S. Pat.* 2,730,297

Experiments at Very Low Pressure

20/II

See Abstract No.: 12/I

Ion Pump

21/II

United States. The pump described consists essentially of a metal envelope comprising three hollow cylindrical sections sealed together lengthwise. The centre section has a side inlet, for connection to the system to be evacuated, and is provided internally with a loosely wound helical coil through which a high current can be passed to produce an axial magnetic field. Each end section has external magnetic windings which extend the field along the pump axis at approximately uniform strength. The cathode assemblies are mounted at the outer ends of these sections, and are maintained at about −500 V relative to the anode envelope. In operation, one of the cathodes is heated so as to discharge electrons, which are collimated into an axial beam by the magnetic field. The electrons, moving in tight helixes around the axis, travel along the pump through the centre coil and on to the second cathode which repels them back along their path. The discharge therefore becomes oscillatory, and the probability of ionisation of gas molecules is very high. The positive ions formed strike the cathodes and are either absorbed there or trapped on nearby surfaces by sputtered cathode material. A con-

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E. O. Lawrence
J. S. Foster Jr. &
U.S. At. Engy. Comm.
U.S. Pat.
2,726,805

stricted portion in front of each cathode ensures that any uncharged molecules formed by recombination, which may migrate towards the inlet, must pass back through the arc and so become re-ionised. A small gas leak may be admitted near one cathode so that the local pressure here remains high enough for the arc to be maintained. The fore pump manifold is connected to a point near each cathode, but is closed off for normal working unless inert gases are to be pumped. The pump is capable of a speed of 6,000 l./s. and a vacuum of 10^{-7} mm. Hg.

22/II
Article by
E. Thomas
Bull. Classe Sci.
42, July 1956
778.783

Study of an Evapor-Ion Pump

Belgium. A vacuum pump working on the principle of the ion pumping of gases and of gettering by titanium which evaporates continuously and condenses on the inner wall of the pump is described. The mechanism for the feeding of titanium is also described. The pump is now on trial.

(*Author*)

23/II

Improvements i.o.r.t. High Vacuum Pumping Devices

United States. The device described is an ionisation pumping apparatus for producing very low pressures. It consists of a glass bulb containing an electrode assembly and having a side tube leading to the system to be evacuated and to the fore pump. Two filaments are provided: One, of tungsten, to act as a source of electrons, and the other, of nickel or similar getter material which can be evaporated readily, to produce a layer on the walls of the bulb. An accelerator electrode, in the form of a helical grid surrounding the filaments, is maintained at about + 125 V relative to the emitting filament. To start operations, the system is first evacuated to about 1 micron Hg with the fore pump while a layer of getter material is evaporated on to the bulb walls. The emitting filament is then switched on, and the electrons given off are accelerated through the grid and ionise the residual gas molecules with which they collide; these ions are driven into the walls of the bulb and absorbed. When saturation is reached, more getter material is evaporated from the second filament so as to form a fresh absorbing surface. If necessary the evaporated layer may be maintained at a negative potential with respect to the emitting filament. During the fine pumping stage the bulb is immersed in liquid air.

D. Alpert &
Westinghouse Electric International Co.
Brit. Pat.
755,074

24/II

Vacuum Container Imcorporating a Hand-Operated Vacuum Pump

See Abstract No.: 149/III

25/II

The Operation of McLeod Gauges and Toepler Pumps

United States. A system is described for the control of the rate of flow of mercury from the reservoir of a McLeod gauge or Toepler pump which avoids the danger of sudden surges of mercury. It consists of two needle valves, one in the line leading to the rough vacuum and the other in the line leading to the atmosphere. Simultaneous adjustment of the two valves permits precise regulation of the pressure in the reservoir. A stopcock is provided between the valves and the reservoir; this is closed when the system is not in use since leakage of the needle valves would allow the mercury to rise if the source of rough vacuum failed.

Article by
M. B. Reynolds
J. Chem. Educ.
32, Dec. 1955
621

21 — GAUGES — 21

26/II

The Operation of McLeod Gauges and Toepler Pumps

See Abstract No.: 25/II

27/II

A McLeod Gauge for Measuring a Wide Range of Pressures

Australia. In this McLeod gauge the closed capillary consists of a length of fine capillary for the measurement of low pressures in the usual manner but between this and the main bulb there is a small bulb connected to the main bulb by a larger bore capillary. A datum line on this capillary is used when it is desired to measure pressures up to several millimetres of mercury. At these pressures, however, it is not permissible to neglect the pressure of the gas over the mercury in the open capillary of a McLeod gauge of normal design. In this McLeod gauge the space above the two capillary tubes, one for each range of the instrument, is isolated from the rest of the system and is kept evacuated by an auxiliary pump. This isolation is achieved by having two concentric tubes leading down to the mercury reservoir, the mercury rising up the inner tube sealing off the bulb and closed capillary from the system, while the open capillary tubes are supplied with mercury through the annular space surrounding the inner tube.

Note by
H. A. Wyllie
J. Sci. Instrum.
33, Aug. 1956
317

28/II

Simplified Method for McLeod Gauge Design and Calibration

United States. The construction of the McLeod gauge is simple but information on the exact size of capillary bore and bulb volume for a desired pressure range is difficult to find. A nomograph has been designed (and is reproduced) which overcomes this difficulty and can be used for the drawing up of specifications to the glass blower, for instance. It is usuable for any McLeod gauge where the mercury in the outside arm is brought level to the sealed top of the capillary tube fixed to the bulb of the gauge and pressure readings are made by the length of the column of gas compressed in this capillary. The nomograph covers pressures between 30 and 10^{-6} mm. Hg and bulb volumes from 10 to 250 cm^3.

Article by
P. Lott
Analyt. Chem.
28, Feb. 1956
276-277

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Permanent Record from a Mercury Manometer

29/II

United States. It is valuable in experimental physiology and surgery to be able to have a continuous and permanent record of blood pressure. This note describes a simple adaptation of a mercury manometer to give an electrical recording. Into one limb of the manometer are inserted side by side a stainless steel rod and a 9H pencil lead, each being about 5 inch. long by $\frac{1}{16}$ inch diameter. The resistance of the lead may be as high as several hundred ohms, and as the mercury rises up the tube this resistance is progressively short-circuited, a linear relation between resistance and length of lead exposed being found. The steel rod serves to make contact with the mercury. A flashlight cell and recording milliammeter complete the equipment. A constant-current supply is also shown for use with a recording voltmeter.

Note by S. M. Ross & E. E. Suckling *Rev. Sci. Instrum.* **27**, June 1956 409

A Direct-Reading Double-Sided Micromanometer

30/II

Holland. A differential-capacitance type of instrument is described, operated with a 500 kc/sec. bridge, the output of which is rectified and used to restore a diaphragm to its null position by electrostatic attraction. The rectified output also indicates the pressure, which may therefore be recorded or used to control some industrial process, *e.g.*, the filling of a vessel to a predetermined pressure. The mechanical design has been described previously (*Appl. Sci. Res.*, **4B**, 1955, 329) and is only given briefly. A stainless steel diaphragm, 2.5 cm. in diameter by 20 micron thick, is clamped with copper gaskets between stainless steel flanges. At either side is fixed an insulated capacitor plate, with electrical connections entering through vacuum seals. The space at one side of the diaphragm is highly evacuated and the other side connected to the unknown pressure. (The use of a Penning gauge to maintain the reference vacuum is suggested). Any displacement of the diaphragm from its equilibrium position unbalances the bridge, in which two arms are small variable capacitors and the other two are made each from two series resonant circuits, interconnected by a screened cable, the whole being symmetrical with respect to earth. One of each pair of resonant circuits is mounted on the measuring head, part of the capacitance of each being formed by the manometer, whose diaphragm is earthed. Any unbalance is amplified and fed to a phase-sensitive rectifier, which gives a d.c. output. This d.c. is fed back to the plates of the manometer so as to tend to return the diaphragm to its zero position; by adding a fixed d.c. voltage, and applying the rectifier output differentially to the two fixed plates of the head, a linear relation between pressure (difference) and output voltage is obtained up to 0.5 mm. Hg. The range can be extended to 20 mm. by disconnecting the feedback and measuring the capacitance changes (50 pF at 10 mm.). The gauge gives an indication which is independent of the gas used.

Article by J. J. Opstelten, N. Warmlotz & J. J. Z. van Zelst *Appl. Sci. Res.* **6B**, 1956 124-136

Simple Sensitive Electrical Pressure Gauge

31/II

United States. A simple, sensitive, electrical pressure measurement device has been constructed which is capable of measuring and recording absolute or differential pressures of corrosive materials of isolated systems. A linear variable differential transformer attached to a sylphon bellows indicates differential pressure across the bellows or serves as a null indicator when an unknown pressure on one side of the bellows is balanced with a gas of measurable pressure on the other side. In order to prevent inelastic deformation, the motion of the bellows is limited to 60 mm. Hg, although larger pressure differential can be measured. The sensitivity is independent of temperature pressure and the device can be compensated for temperature. Absolute pressures and small differential pressures can be measured to ± 0.02 mm. Hg with an input signal of 2 kc, and to ± 0.005 mm. Hg with an input signal of 10 kc. A vacuum tube voltmeter with a full scale of 1 millivolt is used as the output indicator.

(*Authors*)

Article by K. M. Sancier & W. Rickeson *Rev. Sci. Instrum.* **27**, March 1956 134-136

Micromanometer of High Sensitivity

32/II

United States. The instrument was designed for determining small differences in the specific weights of gas mixtures for the purpose of analysis. It consists essentially of a U-tube manometer with vertical arms 1 inch in diameter which are connected at the bottom by a precision bore capillary tube of 0.120 inch diameter. The arms are partly filled with methyl alcohol, and an air bubble is introduced into the centre of the capillary. The gases to be compared are contained in two glass columns 139 inch. high joined to the tops of the U-tube arms. Any difference in the specific weights of the columns then produces a minute change in liquid level in the two arms, and the consequent movement of the bubble, much magnified by the difference in bores, is determined by a lens and vernier scale. The U-tube and the gas columns are immersed in water baths to maintain constant temperatures. For greater sensitivity arms of 2 and 3 inch. bore are also provided, any of which may be selected at will by a system of stopcocks. The highest sensitivity attainable, with 3-inch. diameter arms is 2×10^{-6} inches of methyl alcohol.

Article by S. Lynn, W. H. Corcoran & B. H. Sage *Rev. Sci. Instrum.* **27**, June 1956 368-369

The Pirani Gauge

33/II

United Kingdom. A Pirani gauge for use in supersonic wind tunnels is described. The gauge heads consist of a pair of surgical lamps $\frac{11}{32}$ inch long and 0.082 inch diameter, mounted in a metal block to ensure the same temperature environment. The small size reduces the response time and enables the gauge heads to be mounted close to the pressure orifice with a minimum of connecting tubing. One gauge head is sealed off at atmospheric pressure and provides partial temperature compensation, the two elements being connected in adjacent arms of a constant-current Wheatstone bridge. It is stated that a wet cell battery is a simpler method of obtaining a stable

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current supply than an electrically-regulated supply. Provision is made for switching to a circuit configuration in which the sealed-off head alone is used as a resistance thermometer to measure the temperature of the gauge wall; this enables a correction to be applied to pressure measurements made at a gauge temperature different from that of the calibration. The instrument has been used over the pressure range 0.1 to 10 mm. Hg, the calibration being made against an inclined tube manometer; an accuracy of $\pm$ 2% at pressures up to 4 mm. Hg is claimed. The influence of changes in the accommodation coefficient, lag effects and gas composition on the accuracy of measurement are discussed.

Article by P. G. Morgan *Electr. J.* 156, 22.6.1956 1999-2000

34/II

A Pirani Gauge for Operation up to a Pressure of 10 mm. of Mercury

United Kingdom. The authors describe experiments carried out to study the importance of the length of the wire elements in the Pirani gauge. By supporting a comparatively long straight wire at a number of equidistant points along its length the end losses are increased dependent on heat conduction through the gas at higher pressures, hence the sensitivity falls more slowly with increasing pressures. The experiments were performed using wires of 0.001 inch tungsten welded on to 1 mm. diameter nickel rods embedded in a glass rod in the centre of the glass envelope. The length of individual elements was 1.5, 5.0, 10 and 20 mm., the total number of elements being 10, 10, 4 and 2 respectively. A commercial Pirani gauge of eighteen elements each 60 mm. long of 0.001 inch tungsten was used as a basis for comparison. The measuring circuit was of the conventional Wheatstone-bridge type composed of high stability resistors enabling the resistance of the Pirani element to be measured at all times. Tables are given comparing the five types examined. For different element length, operating temperatures (between 25°C and 400°C) and bridge ratios (between 0.1 and 10.0), the useful range, output voltage (at 90% of saturation) and response time are tabulated. The results show that the operating range is increased by shortening the length of the individual wire elements but the response time is greatly increased (150 seconds in the worst case). The authors discuss the limiting case, where the supports act as small Pirani gauges and influence the temperature pressure characteristics of the wire and reach the conclusion that there is no great advantage to be gained below 1.5 mm. element length using 0.001 inch diameter wire. A useful gauge up to 3 mm. mercury can be made using 10 mm. elements for a mean wire temperature of 50°C and a further extension up to 10 mm. mercury using a 1.5 mm. element length but with a long response time. The low temperature of the wire is especially advantageous where corrosive gases may attack the wires at high temperatures.

Article by J. H. Leck & C. S. Martin *J. Sci. Instrum.* 33, May 1956 181-183

35/II

Article by H. Schlitt *Z. Angew. Phys.* 8, No. 5 1956 216-217

A Thermoelectric Vacuum Gauge

Germany. Details are given of a novel thermo-couple gauge which covers the pressure range of 5×10^{-2} mm. Hg to 3 mm. Hg and has been specially designed to give accurate readings, independent of temperature conditions.

36/II

Article by M. Varicak *C.R. Acad. Sci. Paris* 243, 24.9.1956 893-895

Investigations of the Use of Thermistors for the Measurement of Low Pressures

France. The previous range of application of thermistor vacuum gauges of $1–10^{-3}$ mm. Hg is extended to 10^{-6} mm. Hg by using a bead type thermistor of 120,000Ω/cm. with a temperature coefficient of -0.0412. The output is recorded on a cathode-ray oscillograph. The thermal dissipation surface is increased by placing a tin foil, 1.5 cm. diam. 0.001 mm. thick, in contact with the thermistor. Thermal equilibrium with the wall at ambient temperature is attained in 45 seconds.

37/II

Electrical Clean-Up of Gases

See Abstract No.: 7/I

38/II

Article by R. P. Henry *Le Vide* 11, March/April 1956 54-63

Absolute Pressure Determination with an Ionisation Gauge

France. Reference is made to the method of determining the absolute pressure in a vacuum system with an ionisation gauge designed by C. W. Oatley in *Brit J. Appl. Phys.*, **3**, October 1954. The author reports on a modified version of this technique, employed by himself, using an 'Afnor' ionisation gauge. Applying a correction factor for gas evolution from the walls of the vacuum vessel an accuracy of measurement of about $\pm$1% is possible.

39/II

A Simple and Reliable Ionisation Manometer

Holland. The two essential problems in the design of an ionisation manometer are, the adjustment and stabilisation of the electron current and the measuring of the ion current. In the design described a central grid is placed between the cathode and anode of the conventional manometer. Together, the cathode grid and anode form a triode, the anode current of which can be stabilised by placing a suitable resistance in the cathode circuit. The grid and anode are held at 85 V and 255 V positive relative to earth by means of voltage stabilising tubes. Two values of electron current are used namely 0.5 mA and 2.5 mA, the latter at lower pressures. With these currents the cathode is slightly positive w.r.t. the grid. The cathode saturation emission is adjusted to be 0.5 mA in excess of the actual emitted electron current. The filaments current to give the required saturation

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emission depends on several factors *e.g.*, temperature of the filament which depends on the work function of the cathode metal which is in turn effectd by the type of gas and heat losses from the cathode and these depend on gas pressure and type of gas. The three conditions of the cathode, *i.e.* 0.5 mA, 2.5 mA and saturation emission are indicated by a meter in the cathode circuit and adjusted by means of switching in or out and adjusting cathode resistors. A diagram and circuit are given explaining this in terms of load lines. Measurement of the the ion current is carried out by a method due to Laferti (Dushman. *Scientific Foundations of Vacuum Technique*, 361) where the ion current from the collector is passed through a resistor to earth. The voltage produced across this resistor is applied to the control grid of a pentode E80F which is one of the branches of a Wheatstone Bridge network. The other branches being a similar valve E80F and two resistors. The current through a micro-ammeter across the bridge (between the anodes of the two pentodes) is a measure of the ion current and thus of the pressure. Provision is made in the circuit for adjustment of the bridge such that the zero can be set, *i.e.* no ionising current, and such that the sensitivity can be set by referring the grid of the first pentode to a standard voltage. The grid resistors of both pentodes having always the same values and are adjustable in five steps each differing by a factor of 10, thus giving five measuring ranges. The calibration curves for two manometers, one of 50 c.c. capacity and one of 10 c.c. capacity, show that the current increases more rapidly than in strict proportionality to the pressure. The curves are extrapolated down to 10^{-8} mm. Hg. Improvements in accuracy at low pressures have been made in several ways. The walls of the gauge have been made internally conducting and are earthed, except near the leads, thus eliminating effects due to wall charges. The ion collector is in the form of a wide helix of thin wire in order to minimise the x-ray effect. The three concentric electrodes which are of molybdenum wire are mounted without support in such a way that they may be outgassed by direct current heating, the supply voltages being arranged such that all reach roughly the same temperatures.

Article by E. Bouwmeester & N. Warmoltz *Philips Tech. Rev.* 17, Oct. 1955 121-125

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Improvements i.o.r.t. Ionisation Manometers

40/II

Germany. The patent describes a cold cathode ionisation gauge of all-metal construction and small volume consisting essentially of a rod-shaped anode in coaxial position with a cylindrical cathode, the poles of the magnetic circuit being coaxial with the cathode. The vacuum envelope forms the return path for the magnetic system in which the pole pieces are cylindrical rings between which lies the cylindrical cathode electrically insulated from them by mica discs. To protect the pole pieces from the electrical discharge, which may cause degassing, end caps are fitted to the cathode cylinder with a tube fixed to the centre which protrudes into the bore of the magnets. The anode rod is supported in an insulated bush from one end of the cathode and lies along the axis of the cathode, extending into the bore of the magnet pole pies on the other side as far as the region of minimum field intensity. The rod forming the anode is sleeved with glass from its point of support to the region of minimum field intensity. By these means the discharge is confined to the cathode volume. A spring between one cathode end cap and the mica washer holds the cathode resiliently in position. Holes are drilled in the wall of the cathode to facilitate evacuation of the interior of the cathode. Electrical connection to the cathode is made *via* a small glass-metal seal in the vacuum casing. The gauge is connected to the vacuum system by an O-ring vacuum union.

Siemens & Halske A. G. *Brit. Pat.* 754,515

Improvements i.o.r.t. Devices for Measuring Very Low Gas Pressures

41/II

United Kingdom. The invention relates to a modification of the Alpert pattern of ionisation gauge to enable accurate measurements to be made with simple apparatus. A fourth electrode or anode is introduced lying preferably within the grid electrode of the gauge on the opposite side of the collector electrode to the filament or cathode. The collector electrode which is negative with respect to the cathode deflects electrons from the fourth electrode which is positive. The electron current to the anode depends therefore on the potential of the collector. The collector being a thin wire has only a deflective effect on the electron current. In one embodiment described the grid is a planar grid lying between the collector and the anode. The collector is connected *via* a high resistor to a point of negative potential so that small changes in ion current received by the collector, due to changes in pressure, cause comparatively large changes in collector potential which in turn causes measurable changes in electron current to the anode which may be measured directly or may be compared to the electron current received by the grid. The measuring instrument in this embodiment is connected between grid and anode both of which are connected to points of positive potential through high resistors.

Philips Electrical Industries Ltd. *Brit. Pat.* 757,147

Observations on the Characteristics of the Cold Cathode Ionisation gauge

42/II

United Kingdom. The calibration of a cylindrical anode cold cathode ionisation gauge (Penning gauge) has been made in the pressure range 10^{-5} to 10^{-9} mm. Hg. This has extended the calibration of this gauge to pressure ranges below 10^{-7} mm. where the validity of extrapolation has been questioned. The gauge employed by the authors had nickel electrodes, an anode approximately 1 inch long and 1 inch in diameter, and a spacing between the 1 inch diameter cathode discs and the anode of $\frac{1}{16}$ inch. The gauge envelope was connected by a wide bore glass tube (N_2 conductance 10 l/s). to a Bayard-Alpert type hot cathode ionisation gauge, used as reference. Two liquid air traps separated the gauges from the pumping plant, which comprised two mercury diffusion pumps and a mechanical pump connected in cascade. The pressure in the gauges was controlled by leaking gas through a porous plug into the main vacuum system from an auxiliary reservoir. After baking at 400°C for one hour, and operation of the discharge for one hour at 2,000 V and 600 G, the ultimate pressure was better than 10^{-6} mm. Hg. After ten hours operation at 2,000 V the discharge current had fallen from 100 to

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5 μA, and calibration characteristics were measured for air. The discharge voltage was then increased to 4,000 V, causing an immediate rise to 100 μA but after 200 hours the ultimate pressure reading fell to 1 μA. The calibrations were then repeated. After 10 hrs. plots of gauge current against pressure or voltage showed typical exponential curves. After 200 hrs. the plots were straight lines showing discharge current to be proportional to (*a*) voltage at constant pressure and (*b*) pressure at constant voltage. The gauge sensitivity fell over the 200 hr. period, but calibration curves remained stable thereafter. Further extensive baking enabled the range 10^{-9} to 10^{-7} mm. Hg to be investigated. Straight line current-pressure characterisitics were obtained in this range, but a sharp discontinuity with a sudden fall in current was observed at about 10^{-8} mm. Hg. The results indicate a change in the nature of the electrodes during the first 200 hrs. operation. One explanation may be the deposition of a carbon layer on the cathode surfaces, which has been observed all through the experiments.

Note by J. H. Leck & A. Riddoch *Brit. J. Appl. Phys.* 7 April 1956 153-155

43/II

Penning Gauge as Leak Detector

See Abstract No.: 114/II

22 — MEASURING PLANT (VACUUM) — 22

44/II

Optical Instruments for the Vacuum Ultra-Violet

See Abstract No.: 110/I

45/II

Vacuum Research and the Mass Spectrometer

United Kingdom. Despite the widespread use of various vacuum techniques many of the basic phenomena observed in routine applications are not well understood. The investigation of these processes either in specially designed experiments, or by observations on standard plant is assisted if the partial pressure of a single gas can be measured when others are present. This is possible by several methods, but mass-spectrometric analysis is by far the most general and convenient technique. The suitability of various mass spectrometers for vacuum studies is discussed and illustrated by reference to accounts of experimental work. Particular attention is given to certain new types and an attempt made to assess their potentialities in this field.

Article by A. G. Edwards *Vacuum* 5, Oct. 1955 93-108

46/II

Compound Ion-Resonance Mass Spectrometer

United States. A new mass spectrometer is proposed which consists essentially of a low resolution 180° instrument and a cyclotron in series. Its advantages over the classical cyclotron, the omegatron and the mass synchrometer are its freedom from space-charge effects, discrimination, and gas scattering; in signal available and in the possibility of differential pumping. It retains the characteristics of having a fine resolution depending only on instrument parameters and the e/m of the ion involved. The working principle of the new instrument is explained in detail. Using a symmetrical square wave as the gap voltage the resolving power is moderate but resolving powers of several thousand are theoretically possible with sine wave voltages, but only with a corresponding loss of efficiency. Since the ionisation region in this instrument is physically and electrically separate from the resolving system, a high degree of differential pumping is possible between the latter and the ion source.

Article by C. F. Robinson *Rev. Sci. Instrum.* 27, Feb. 1956 88-89

47/II

Servo Controlled Leak for Mass Spectrometer

See Abstract No.: 105/II

48/II

Modern Methods of Leak Detection

See Abstract No.: 21/I

49/II

Leak Detector

See Abstract No.: 110/II

50/II

Small Angle X-Ray Diffraction Unit

Australia. A small angle x-ray diffraction unit consisting of a rotating anode x-ray tube and an evacuated x-ray camera is described. The x-ray camera can resolve a spacing of 1,000 Å with a separation of 2 lines per mm. at the x-ray film. Photographs of the first twelve orders of moist collagen have been obtained, fully resolved, with exposures of less than one hour.

(*Author*)

Article by C. R. Worthington *J. Sci. Instrum.* 33, Feb. 1956 66-69

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Mechanically Sealed Beryllium Windows for Permanently Evacuated X-Ray Tubes 51/II

See Abstract No.: 102/II

Chemical Analysis of Thin Films by X-Ray Emission Spectroscopy 52/II

See Abstract No.: 157/I

Microscopy With X-Rays 53/II

United Kingdom. Three types of x-ray microscope are considered. An advantage of using x-rays instead of visible light is that they have a shorter wavelength and can give a higher useful magnification. Their great penetration should also make it possible to examine the interior of objects opaque to light. A reflection-type x-ray microscope has been made in which the rays are focused by a system of cylindrical mirrors. The preparation and alignment of the mirrors are difficult, however, and this type of microscope is not yet a practical research tool. The two other methods are developments of x-radiography. In one, the contact method, the specimen is laid on a collodion film directly on a photographic plate and is irradiated with x-rays. A very small image is obtained which must be either enlarged photographically or inspected under a high power optical microscope. Unless the specimen is very thin by nature, sections 1–100 μ thick must be prepared. Recording emulsions of the finest grain are necessary and the optical microscope must have a resolving power greater than this grain size. A normal x-ray tube can be used in the region just beyond the range of the unaided eye but a tube with a smaller focal spot (0.3 mm. dia.) is necessary for resolving fine detail. A suitable low-voltage x-ray tube has been designed by Engstrom in collaboration with the Philip's laboratories at Eindhoven. A recording microphotometer with a spot as small as 2–3 μ dia. has been constructed for use with the x-ray tube and has made it possible to determine the amounts of specific elements present in a specimen. The best resolution obtained with this instrument is of the order of 1 micron. It has been used to measure the distribution of dry weight in nerve cells and nerve fibres and in cytochemical studies of giant chromosomes. Some work has been carried out on living tissues. In the second radiographic method, the projection method, a specimen is placed close to a source of x-rays and a magnified image is thrown on to a fluorescent screen or photographic plate. A special x-ray tube is required since the resolved detail depends on the size of the focal spot which must have a diameter of 1 μ or less. Normal x-ray emulsions can be used. In an instrument of this type developed at Cambridge a small focal spot is obtained by using electromagnetic lenses to form a reduced image of the electron source which is a hot tungsten hairpin. The target emitting the x-rays is a thin metal foil which is sealed into the end of the x-ray tube. The specimen can be brought to within 1/1000 inch of the target and this closeness permits a direct magnification of more than $\times$1,000 in a camera length of only 1 inch or so. The best resolution obtained so far with the instrument approaches 1,000 Å. A limit is set according to how small the focal spot can be made without losing too much intensity. Relatively bulky specimens, for example complete insects, can be used and stereo-pictures giving a 3-dimensional view can be obtained by tilting the specimen between exposures. The various elements present in mixtures or tissues can be identified. Projection micrographs are shown of an aluminium tin alloy (magnification $\times$350) and of an aphid body (magnification $\times$80). The technique of this instrument is similar in some ways to that of the electron microscope but the apparatus is smaller and less complex. It is also possible to work with specimens in air in the natural wet condition and even in the living state. Two commercial versions of the laboratory model are being developed.

Article by V. E. Cosslet & W. C. Nixon *Times Sci. Rev.* Winter 1955 10-11

The Automatic Recording of Electron Diffraction Patterns Applied to the Study of Evaporated Copper Layers 54/II

United Kingdom. An apparatus has been constructed which successively records complete electron diffraction patterns after pre-set time intervals. This has been used in conjunction with a reflection specimen furnace of new design in the study of the growth of copper evaporated on to flat (111) silver surfaces.

(*Authors*)

Article by R. B. Kehoe, R. C. Newman & D. W. Pashley *Brit. J. Appl. Phys.* 7, Jan. 1956 29-31

An Emission Electron Microscope for Research at High Temperatures 55/II

Holland. An emission electron microscope is described which has a resolving power of about 1,000 Å and an (adjustable) magnification of up to $\times$3,000. After a brief review of the theoretical and practical limitation of the resolving power by electron-optical considerations, the nature of the objects to be examined is discussed in greater detail. Since this microscope is primarily intended for the investigation of metals at high temperatures, thermionic emission is used. Activators such as barium or caesium evaporated on to the surface of the object, ensure adequate emission in temperature ranges of practical interest, and likewise produce differential emission from the variously oriented grains of a polycrystalline metal (contrast). The construction of the cathode permits the use of four different activators while the microscope is actually in use, scanning of wide areas of the object surface and variation of the degree of magnification by adjusting the field of the first electron lens (an electrostatic 'immersion lens'). Apart from this lens, the electron-optical system employs two magnetic lenses, the second of which is practically identical with the projector lens of the transmission electron microscope EM 75 kV and, as in the latter, permits variation in the magnification. The emission microscope resembles the EM 75 kV, in many other details of its construction. Nevertheless there are fundamental differences in the vacuum system and the system for stabilising the accelerating voltage of 45 kV. The demands made on both the vacuum system and the voltage stabilisation are far higher for the emission microscope than for the transmission microscope.

(*Authors*)

Article by G. Baas & G. W. Rathenau *Philips Tech. Rev.* 18, June 1956 1-10

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56/II
Article by J. A. Becker & R. G. Brandes
J. Appl. Phys. 27, March 1956 221-223

A Favourable Condition for Seeing Simple Molecules in a Field Emission Microscope

United States. It has been shown theoretically that irregularities on a metal tip cause increased local resolution in a field emission system. The paper presents experimental evidence supporting the theory. Baking the system at about 350°C is believed to have caused irregularities in the tungsten tip by the etching action of water vapour and spots were observed on the screen. That irregularities were present was deduced from the voltage-current characteristics of the system. It has also been shown that adsorbed molecules give bright spots on the screen.

57/II
Article by W. P. Dyke & J. P. Barbour
J. Appl. Phys. 27, April 1956 356-360

Pulsed T-F Emission Electron Projection Microscopy

United States. High-temperature high-field emission microscopy suffers from the drawbacks of cathode instability and the effects of electrostatic forces on the mechanisms being observed. By pulsing the system at low duty cycle (1 μ sec. pulses at 30 pps.) these effects are made negligible. The apparatus has been described elsewhere and enables observations to be made of a number of phenomena and under various conditions which are not possible using a steady field. Examples are given of volume diffusion followed by surface migration of impurities in the cathode, condensation and surface migration of barium, and the relative movement of the cathode surface and twin boundary in the cathode material. Cathode distortion and the high steady fields in the normal method would not allow the observation of these effects.

58/II
Article by E. W. Muller
J. Appl. Phys. 27, May 1956 474-476

Resolution of the Atomic Structure of a Metal Surface by the Field Ion Microscope

United States. Work is described on the field ion microscope, developed from the field emission microscope in which electrons emitted from a point electrode at a high potential are received on a fluorescent screen. In the apparatus described, the point is positive and a gas filling at a few microns pressure (He is preferred) gives rise to ionisation of some of the gas molecules which approach the point, and the fluorescent image is formed by the ions. Theoretical discussion of the factors affecting the resolution shows the importance of a gas with a low polarisability. In the apparatus described, the point is of tungsten, protruding from the inner wall of what is essentially a Dewar vessel. The point can thus be cooled by filling the vessel with liquid N_2 or H_2 and further cooling of the gas is obtained by surrounding the inner vessel by an annular space which can also be filled with refrigerant. This drastic cooling increases the accommodation coefficient of the gas, so that the ions formed from the rebounding molecules will have substantially the temperature of the point and a correspondingly small transverse kinetic energy. It is estimated that using a point of 1,000 Å radius and He gas, the theoretical diameter of the scattering disc is reduced from 6 to 1.5 Å by cooling. Photographs taken under these conditions show a large increase in resolution compared to a similar image formed by electrons. In many parts of the pictures the individual atoms constituting the concentric edges of the (011) net planes are resolved. Field evaporation (at liquid H_2 temperature and a field of about 5.7×10^8 V/cm) is found to produce a much more perfect surface than annealing. Work is in progress observing the damage caused by ion bombardment, etc., and various kinds of dislocations have been found. Their extension into the depth can be analysed by controlled evaporation of the surface layers.

59/II
Article by V. E. Cosslett & R. W. Horne
Vacuum 5, Oct. 1955 109-130

Recent Developments in Specimen Preparation Techniques for Electron Microscopy

United Kingdom. Present-day methods employed in the preparation of specimens for examination in the electron microscope are reviewed. After discussing the properties required of the specimen supports and mentioning the standards available for a critical assessment of the micrograph the authors describe microtomes available for ultra-thin sectioning, staining techniques, freeze drying techniques, and various replication methods employed in the preparation of specimens of biological materials. Special mention is made of the use of the recently developed techniques for the deposition of carbon films. In the second part of the paper the authors investigate the present techniques employed for the specimen preparation of inorganic materials, in particular the crystalline structure and surface conditions of metals. Silicon monoxide replication methods are mentioned in connection with the preparation of specimens for chemical studies and certain aspects of the specimen preparation of fibrous materials are mentioned.

60/II

A Simple Adaptation of the Carbon Replica Technique for the Examination of Selected Areas in the Electron Microscope

United Kingdom. The paper describes an improved method of preparing carbon replicas which makes it possible to examine areas or features which have been selected previously in the optical microscope. The method is simpler than those previously devised and requires only an attachment to a 16 mm. optical microscope objective. This consists of a flat plate, drilled so that it can be clamped between the objective cap and the main body of the microscope, which supports a second plate by a hinge at one end and a hinged bolt at the other. The rotation of a screw on the bolt enables the separation of the plates to be varied. Three small pins are fixed underneath the bottom plate round a small hole which lies on the optical axis of the objectives; these support the specimen grid which is attached with a suitable adhesive. Provision is made for placing a reference scratch on the specimen by means of a printed diamond or sapphire mounted on a lever pivotted from the fixed portion of the microscope stage. After marking the specimen, it is removed from the optical microscope and coated with a thin film of Formvar. It is then returned to the optical microscope and the selected area is located again using the ordinary objective. This is next replaced by the objective modified as above and with a specimen grid

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in position just above the focal point of the microscope. After bringing the selected area under a grid square the microscope column is lowered so that the grid is pressed against the specimen by the pins. The grid is anchored in this position by a few drops of 1–2% Bedacryl and the grid is then separated from the metal. A thin layer of carbon is next deposited on the structure surface of the Formvar and the latter is dissolved away in chloroform leaving the carbon film still attached to the grid and ready for examination in the electron microscope. If the specimen is to be shadowed this must be done through the grid bars and this limits the angle of shadowing to 3:1. A more complicated method is also described which overcomes this difficulty and also gives better results with heavily-etched steel surfaces.

Paper by D. E. Bradley *Brit. J. Appl. Phys.* 6, Dec. 1955 430-432

Direct Carbon Replicas from Metal Surfaces

61/II

United Kingdom. Two methods have been developed for the removal of carbon replica films directly evaporated on to etched metal surfaces. These involve either electropolishing or chemically etching after deposition of the carbon. The film removed by electropolishing gives a replica of high resolution, whilst with the etching technique extraction replicas may be prepared from multi-phase alloys and the extracted phases identified by electron diffraction. Some examples of the application of the techniques to carbon and alloy steels are given.

(*Authors*)

Article by E. Smith & J. Nutting *Brit. J. Appl. Phys.* 7, June 1956 214-217

Use of Carbon Replicas in the Electron Microscopy of Yeast Bud Scars

62/II

United Kingdom. The author has used his two-stage Formvar-carbon technique to obtain shadowed carbon replicas of yeast budding scars. Ultraviolet photolytic methods had shown the existence of budding scars of circular outline, and it has been claimed that two forms of scar exist. This has been confirmed by the present work and two types of scar can be very readily distinguished. The cells are washed, mounted on Formvar films, and a thin layer of carbon is deposited by vacuum evaporation. After dissolution of the Formvar and yeast, the carbon replica is shadowed. The results demonstrate the potentialities of carbon replica techniques in the examination of surfaces of bacteria and other organisms, and more detailed study of yeast bud scars is in progress.

Letter by D. E. Bradley *Research* 8, Dec. 1955 S62-S63

Electron Microscope Observations of Periodicities in the Surface Structure of Tobacco Mosaic Virus

63/II

United Kingdom. The surface structure of tobacco mosaic virus has been investigated in an electron microscope at magnifications of $\times 40{,}000$ and $\times 80{,}000$ using the carbon replica technique. Evidence was found for a longitudinal structure running the full length of the virus rod. Some rods also showed a 'herring-bone' structure; measurements from prints enlarged to $\times 400{,}000$ gave a mean value of 46 Å for the axial repeat-distance of this structure, which is almost exactly double that of the pitch of the helical structure previously deduced from x-ray data. In the few rods which showed evidence of helical structure, the angle of advance was found to be between 80° and 85°, as compared with the value of 82.5° required by the model proposed by Franklin. The width of the rods was found to be 150 ± 5 Å. It was also found that the rods have an angular appearance in cross-section, suggesting a hexagonal form with a groove at the corners.

Letter by R. E. F. Matthews, R. W. Horne & E. M. Green *Nature* 178, 22.9.1956 635-636

Fine Structure of Tobacco Mosaic Virus

64/II

United States. This study was directed at increasing the visibility of macromolecules in the electron microscope, in particular by evaporating heavy metals at angles (with respect to the substrate) close to 0°. A suitably prepared sample of the *U*1 strain of tobacco mosaic virus was sprayed on to the collodion-covered convex face of a plano-convex lens of 250 mm. radius of curvature. Thorium was evaporated from a tungsten filament to give grazing incidence near the pole of the lens. The collodion was then stripped from the glass and mounted on copper grids; this technique gave a range of angles of incidence of the thorium atoms. It was found that rods lying parallel to the incident beam, at angles of incidence near 0°, showed a periodic density variation along the longitudinal axis; the period of these fluctuations averaged 136 Å. The individual striations are not perpendicular to the long axis, and the net effect is that of a right-handed helix. From the variation in contrast as a function of shadowing angle, it can be deduced that the slope of the discontinuity responsible for the striations must be no more than a few degrees and that the height of the discontinuity is of the order of 15–30 Å. Similar results have been obtained for the *U*2 strain of virus.

Letter by R. F. Baker *Nature* 178, 22.9.1956 636-637

A Study of the Formvar Replica Process

65/II

United Kingdom. A detailed study has been made of Formvar replicas of various depths of structure. Plain replicas, shadowed replicas and replicas shadowed on the back surface were prepared from the same area of a metal surface. In order to measure the height of structure which may have penetrated the replica, measurements were made with a reflection interferometer microscope in addition to the normal electron microscope micrograph. Details of the interferometer microscope measuring technique are given. The particular instrument had a resolution slightly better than that given by an ordinary 4 mm. objective. Monochromatic illumination of 5,780 Å was used indicating a height difference of 1,930 Å on the specimen in a displacement of the fringe system by one fringe width. In view of the resolution of this instrument the specimen structure had to be comparatively coarse. Four specimens of pearlitic steel were used and prepared by mechanical polishing and acid etching alternately, until the flowed layer was removed, and were then given final etches of 20, 10, 5 and 2 s respectively in 1% nital. This treatment resulted in heavy, normal, light and invisible etches respectively,

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when examined under the optical microscope. The Formvar film used in replication was invariably of a thickness of 700 Å ±10%, and was prepared by a method described by the authors previously. In this connection it is mentioned that replica films of this kind are normally thicker than generally assumed. A film showing the typical blue coloration is up to 1,000 Å thick and only films about 400 Å thick are practically colourless. Electron micrographs and interferometric examination yielded the qualitative information on the structure penetrating the Formvar film given in a table reproduced below. Resolution of the film thickness employed

Effect of Structure Height on Replica Reproduction

Specimen Number	*Etch Time (s)*	*Average Structure Height on Specimen Surface* Å	*Structure Penetrating the Replica Film*
1	20 (heavy)	1,600–2,000	All details except finest.
2	10 (normal)	1,000–1,600	All details except finest.
3	5 (light)	500–800	Large grains only.
4	2 (invisible)	200–300	Very little; a few large grains just detectable by interferometry.

Article by A. W. Agar & R. S. M. Revell *Brit. J. Appl. Phys.* 7, Jan. 1956 17-25

by the authors was better than 200 Å. When the replica was shadowed this was improved to better than 100 Å, and the authors believe that the best resolution obtainable is probably about 25 Å. Generally, the authors come to the conclusion that an approximately true negative replica of the surface is only formed in the rare cases when the thickness of the film is more than double the depth of the structure replicated. However, in spite of this, Formvar replicas are suitable for many classes of work.

66/II

Production, Properties and Applications of Silicon Monoxide

See Abstract No.: 153/I

67/II

The Production of Transparent Profiles of Dust Particles as an Aid to Automatised Particle Counting

See Abstract No.: 124/II

68/II

A Quartz Fibre Microbalance for Use Inside an Evacuated Container

United Kingdom. The microbalance described measures differences in mass of 10^{-8} g, and can determine μg. amounts of material with an accuracy of 1% in a vacuum or in non-corrosive gases under controlled conditions of temperature and humidity. A fused quartz beam is used with two vertical 5μ dia. quartz suspension fibres placed $\frac{1}{4}$ inch apart to prevent the boat and weight stirrup from rotating out of position during a weighing operation. An experimental type of beam having a vertical, central, 5 μ dia. support fibre is also being considered. The torsion fibre (25 μ dia.) is connected to a circular scale with 400 divisions through a 50:1 reduction gear. A spring loaded anti-backlash gear wheel is used. The working length for one revolution is 2×10^4 divisions~0.6 mg. and the weighing range is ±1 mg. The response per unit mass, or sensitivity, and the minimum mass detectable, or sensibility, can be varied by varying the gear wheel ratio and the thickness of the fibre. A locking device is used to adjust the beam torsion. The index fibre (5 μ dia,.) is illuminated and observed by a modified, standard prismatic optical microscope placed with its objective about 1 cm. away from the index fibre. The microscope is focused, and balancing is carried out by rotating the torsion head unit until two index fibre images, one from each end of the beam, appear to be in a straight line. A successive series of weighings can be made from eighteen weighting boats which are suspended from notched teeth on a circular loading tray. When the tray is lowered it is located by a pin passing up through one of eighteen holes in the top index dial so that any required boat can be transferred to the scale pan for weighing and then back to the tray. A similar notched platform carries three sets of weights in the form of platinum riders. There are nine weights 0.001 g. to 0.009 g., nine weights 0.01 g. to 0.09 g. and one weight 0.1 g. One weight from each set is lowered on to a three-tiered stirrup by means of a selection device outside the case. This device consists of three adjustable slotted cylinders which may be set to give the required loading. The balance can only be loaded or unloaded when a shaft-locating pin passes through each cylinder slot. This ensures that all weights are removed after a weighing and facilitates weight checking. An unknown mass is determined with weights to the nearest mg. and then the torsion head is used for the final reading. The balance unit is housed in a $\frac{1}{4}$-inch thick Pyrex cylinder 12 inch. × 9 inch. The edges of this cylinder are ground flat and rest on L-shaped rubber gaskets in grooves cut in two $\frac{3}{8}$-inch brass end plates so that the unit may be used at very low pressures, and may also be lowered into a thermostat. The various $\frac{1}{4}$-inch dia. polished steel shafts pass through Wilson vacuum seals attached to the brass plates. A stirrer is fixed inside the apparatus. The instrument can be calibrated in terms of a known mass by the usual methods.

Report by W. P. Hutchinson *A.E.R.E. Rep. No. C/R* 1757 October 1955

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Magnetic Suspension Balance

69/II

United States. It is sometimes necessary to weigh materials inside a vacuum chamber or in a gas other than air or in a liquid or vapour. The magnetic suspension balance can perform such weighings and it also provides a reliable method of studying the adsorption of gases on to surfaces. The material to be weighed is attached to a steel sphere which is freely suspended within a vacuum-tight glass chamber by the axial magnetic field of a solenoid. The horizontal position of the sphere is stable due to the symmetrically diverging magnetic field of the solenoid; its vertical position is determined by the solenoid current which is controlled by a servo-loop actuated by a light beam. Light from a narrow horizontal slit is focused on to the upper surface of the sphere. Part of the beam is scattered by the sphere and some of this light is conducted to a photomultiplier by a 'light pipe'. The amplified output of the photomultiplier controls the power valves supplying the current for the solenoid. When the circuit is correctly adjusted the sphere appears perfectly stationary when viewed through a $\times 100$ microscope. The light not interrupted by the sphere is focused on to a second photomultiplier. When the mass of the sphere is changed by the addition of material to be weighed or through adsorption, it takes up a new stable position. Its change in height is a measure of the change in weight and this is determined by finding the change in current necessary to bring the sphere back to its previous position. The second photomultiplier circuit acts as a sensitive height indicator. The limitation in the sensitivity of the instrument lies in the natural fluctuations of the servo system. The smallest mass changes that have been recorded were of the order of 5×10^{-11} grams with a total suspended weight of 2.3×10^{-6} grams. Masses varying from 10^{5} grams to about 2×10^{-6} grams have been suspended. Calibration can be carried out directly by making use of the buoyancy effect of a gas surrounding the suspended body. Calibration remains constant from day to day if reasonable care is taken. The authors give a simple theory for the instrument and describe the application of the balance to measure the adsorption of nitrogen and helium on to a sphere plated with copper, silver and nickel at pressures down to 0.1 mm. Hg.

Article by J. W. Beams, C. W. Hulburt, W. E. Lotz, Jr. & R. M. Montague Jr. *Rev. Sci. Instrum.* **26**, Dec. 1955 1181-1185

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Modifications to an Air-Driven Ultra-Centrifuge

70/II

Australia. A temperature rise of 3 to 4°C per hour was observed in the rotor of a model 1948 Phywe ultra-centrifuge running at 45,000 r.p.m. in pure hydrogen at 3 mm. Hg. This heating was attributed to frictional heating of the rotor passing through the hydrogen and to heat generated by friction in the small stabilising ball bearing in the base of the rotor. Operation of the centrifuge at $2-3 \times 10^{-4}$ mm. Hg and removal of the stabilising ball race from the rotor to a water-cooled housing underneath reduced the temperature rise to 0.5 to 0.6°C per hour at 50,000 r.p.m. Constructional details of the bearing modifications are given.

Note by I. J. O'Donnell *J. Sci. Instrum.* **32**, Oct. 1955 402-403

On the Dynamic Temperature Response of a Vacuum Calorimeter

71/II

See Abstract No.: 124/I

26 — MATERIALS — 26

Some Aspects of Handling Mercury

72/II

United Kingdom. An account is given of some problems attached to the handling of mercury in large quantities. The account is based on personal experience by the author, and restricted to matters where the author has first-hand practical knowledge. The toxicity and vapour pressure, as well as the mechanical and chemical behaviour of mercury, are dealt with, essentially from the point of view of the safey of the personnel. The general layout of mercury laboratories is discussed and mention is made of the special requirements with regard to plant and instrumentation, furniture and fire hazard equipment. Existing vapour detection apparatus is described in detail and a brief survey is given of the methods of flow measurement employed by the author.

Article by J. G. S. Biram *Vacuum* **5**, Oct. 1955 77-92

Improved Method for Cleaning Mercury

73/II

United States. Describes a technique combining oxidation and dissolving of contaminants with filtration through small holes to remove surface dirt. A 500 c.c. separating funnel feeds the mercury into a piece of soft rubber hose (5 mm. diameter, 1 mm. wall) which is closed by a plug and pierced with fine holes. The funnel is fitted through the bung of a large bottle containing 10% nitric acid, so that the mercury emerges through the holes into the acid as a fine spray. At the same time, a stream of filtered air is drawn through the acid by means of a filter pump and two tubes, one of which has a 4 mm. orifice positioned near the bottom of the bottle so that the bubbles scatter the Hg spray. Individual droplets of Hg have a path of the order of 80 cm. in acid, supersaturated with air. The apparatus cleans 500 c.c. of Hg in about 4 hours with no attention after first setting the stopcock of the funnel.

Note by N. Fuschillo *Rev. Sci. Instrum.* **27**, June 1956 410-411

A Mercury Safety Valve for Electrolysis of Heavy Water

74/II

See Abstract No.: 95/II

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75/II

The Cubic Form of Ice

United Kingdom. Electron diffraction experiments have been carried out to study the crystalline forms of ice in deposits from water vapour effected on substrates kept at various low temperatures. A special low-temperature unit, fitting the electron diffraction camera and consisting of a liquid air jacket containing channels for the electron beam and for the water vapour supplied by a specially constructed injection unit carried the specimen support. The latter was mounted on a brass disc connected both to a heater and the liquid air jacket, facilitating accurate control of the specimen temperature between −180° and +20°C. Substrates used in transmission experiments were Formvar Collodion, silica, amorphous germanium; in reflection experiments, cleved galena or more usually evaporated silver on mica. Three types of diffraction pattern were found as shown in a table reproduced below.

Temperature of Base	*Diffraction Pattern*	*Comments*
−180° to −140°C	Diffuse rings	—
−140° to −120°C	Sharp rings	Diamond-type cubic
> −100°C	Sharp rings	Hexagonal ice
> −105°C		Rapid evaporation

Letter by N. D. Lisgarten & M. Blackman *Nature* 178, 7.7.1956 39-40

76/II

Improvements r.t. Detection of Change in Moisture Content of Desiccant Material

United Kingdom. The use of reclaimable desiccant materials, such as silica gel or activated alumina, poses the problem of replacement of the material before it becomes saturated. Either the desiccant is replaced frequently as a matter of routine when it may still be active, or an indication of the degree of moisture uptake is obtained by weighing. Both methods necessitate removal for observation. The patent describes a procedure which permits the observation of moisture uptake by measurement, *in situ*, of the change of dielectric capacity of the desiccant. The desiccant is totally or partially enclosed between two metal electrode surfaces, one of which may be the outer casing of a cylinder or box or tray, and the other an inner concentric cylinder, or set of vanes or lid, conveniently in the form of gauze. These two surfaces form a capacitor which may be connected to a Weatstone bridge circuit. One lead only is necessary if one side of the capacitor and the bridge are earthed. Variation of the moisture content alters the capacitance, which may be measured or used to operate an audible or visible signal. Satisfactory results were obtained with a capacitance of 130 μμF using dry silica gel. The apparent dielectric constant of 3.1 changed to 7.2 on becoming saturated.

G. E. J. Palmer & British Thomson Houston Co. *Brit. Pat.* 748,462

77/II

Study of the Absorption, in Km Waves, of Gases Adsorbed by Silica Gel or Titanium Oxide

France. The work reported has been undertaken in order to study how the dielectric properties of a solid alter as result of adsorption phenomena on the surface. In the course of these studies the variations of the absorptions ε'' have been determined as a function of the temperature, the frequency applied, and the quantity of material adsorbed. Reference is made to studies initiating this work carried out by the author in 1955. The measurements were taken in an experimental apparatus which is illustrated. The determination of ε'' permits the calculation of the activation energy U from the following expression:

$$V_0 = A \exp(-U/KT)$$

The silica gel used in the experiment is marketed under the name of 'Actigal' by Messrs. Prolable and has a specific surface area of the order of 800 sq.m./g. The frequencies applied ranged from 0.1 to 1,000 kHz. The following materials were used as sorbates: C_2H_5Cl, NH_3, C_4H_{10} and water. Details of the results are given in graphs. The value of the activation energy determined by the author for 'pure' silica gel of the make mentioned is 0.34 eV. Certain results are also given of adsorption experiments on titanium oxide, which was non-porous. Using the same sorbates, silica gel shows dipolar Debye absorption whereas titanium oxide does not.

Article by M. M. H. Waldman *J. Phys. Radium* 17, May 1956 426-429

78/II

Multilayer Adsorption on Plane Surfaces by Capacity Measurements I. Adsorption on Glass at High Relative Pressures

Israel. This paper describes an investigation of the physical adsorption of water vapour and isopropyl alcohol on plane sheets of glass, using the change in electrical capacity to determine the thickness of the layers. This method is sufficiently sensitive to enable a small surface area (about 10 sq.cm.) to be used, rather than systems of high specific surface area associated with the use of powders, etc. In the latter case, there is uncertainty about the state of the surface and capillary condensation occurs in addition to surface adsorption. The adsorbent consisted of two microscope cover glasses, each cemented to a slightly larger brass plate 5 mm. thick. After cleaning the surface of the glass, the plates were clamped on two Teflon spacers positioned at the ends beyond the glass. The distance between the glass plates (about 0.6 mm.) was estimated by filling the space between them with amyl alcohol and weighing. The condenser was enclosed in a glass vessel that could be evacuated or is connected to a second vessel containing a solution of known vapour pressure. The electrical circuit consisted of a crystal-controlled oscillator in which the capacity to be measured formed part of the anode circuit. Changes in capacity were measured by compensating them with a precision condenser. The system was stable to better than 0.002 μμF. during 30 minutes, after a 1-hour warming-up; this enabled the layer thickness to be measured to within a few Angstroems. The method of calculating the layer thickness from the change of capacitance is described. Layer thicknesses up to several hundred Angstroems were observed at relative pressures from 0.5 to 0.9976 for water vapour and 0.2 to 0.993 for isopropyl alcohol.

Article by U. Garbatski & M. Folman *J. Phys. Chem.* 60, June 1956 793-796

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Outgassing of Glass

79/II

United States. It is well known that where glass is heated *in vacuo* a rapid evolution of gas (primarily water vapour) occurs upon first heating, followed by an evolution which becomes increasingly persistent as the bake-out temperature approaches the softening point of the glass. The major part of the initial evolution has been attributed to the gases adsorbed on the surface while the persistent evolution at higher temperatures has been attributed to diffusion from the interior. The purpose of this investigation was to separate these two outgassing processes and to provide data for calculating the amount of water which will diffuse from the glass for any time-temperature conditions, following any bake-out in which the surface gases are removed. The apparatus consisted of a fused quartz container in which a sample of known surface area was placed. The sample was usually in the form of a hollow or solid tube. The gas liberated on baking was collected between mercury cut-offs in a gas analysis system. The pressures of permanent gases were measured by a McLeod gauge and those of vapours by a Pirani gauge. Provision was made for collecting samples of the gases for mass spectrometer analysis. The experiments showed that, in all cases, over 98% of the gas evolved was water vapour. At temperatures above 300°C for a soda-lime glass it was found that the water diffusing from a unit surface at constant temperature was linearly related to the square root of the time of bake-out, that is,

$$V = m\,t^{\frac{1}{2}} + s$$

where V is the water evolved per unit area, t is the time of bake-out, and m and s are constants. Thus the intercept of the linear plot is a measure of the water adsorbed on the surface and the slope is a measure of the rate of evolution of water which has diffused to the surface from the interior. The value of the diffusion constant for water at various temperatures and the concentration gradients after bake-out in a soda-lime glass have been calculated from the data and Fick's law of diffusion from a semi-infinitive body. Since the concentration gradient depends only on the volume of water removed, and the linearity of the $\sqrt{t}$ relationship persists for so long, it is possible to calculate the amount of water differing from glass after an arbitrary bake-out. Good agreement is obtained between the calculated and observed results. Data for various glasses are given in tables. One of the tables is reproduced below.

Calculated and Observed Values of Water Evolution from No. 0800 *Glass in Successive Time Intervals at* 450° *After a Preliminary Bake-out at* 480° *for* 0.5 *hour.*

Time at 450°	*Micron (Hg)-liters at* 25° *per sq. dm.*	
	Calc.	*Obs.*
First hour	1.7	1.5
Next hour	1.4	1.2
Next hour	1.2	1.2

No. 0080 is the Corning Glass Works Code number for one of its soda-lime glasses.

Article by B. J. Todd *J. Appl. Phys.* 26, Oct. 1955 1238-1243

How to Build and Use Glass Evaporation Plant

80/II

See Abstract No.: 79/III

Method of Bonding and Article Thereby Formed

81/II

See Abstract No.: 62/IV

Utilising Plastic Impregnation in Equipment for Nuclear Research

82/II

United States. Polyester and epoxy resins are useful in the preparation of magnets, coils and vacuum equipment. They provide high mechanical strength and good electrical properties, and their characteristics allow them to be used at pressures down to 10^{-6} mm. Hg. A particular advantage is that they lend themselves to techniques requiring little tooling, and they are therefore useful when only one or two items are to be prepared. Vacuum equipment may be built up by hand of layers of cotton tape impregnated with the plastic. Coils may be insulated and bonded together also using tapes and plastic, while magnet laminations may be bound together using the plastic as an adhesive. Before curing, it is sometimes necessary to remove air bubbles from the plastic by placing the work in a vacuum chamber.

Report by W. W. Salsig, Jr. *A.E.C. Rep. No.* UCRL.3195 December 1955

Method of Coating Polytetrafluoroethylene Articles and Resulting Articles

83/II

United States. The invention describes processes by which unsupported films of polytetrafluoroethylene (PTFE) and articles made of PTFE may be coated by a securely bonded thin metallic layer. The methods used hitherto for coating the inert waxy surface of PTFE with a metallic layer have been unsatisfactory in many respects, giving quite thick poorly conducting coatings, not readily removable. The process now described deposits the metal by vacuum evaporation on to porous self-supporting films of PTFE, obtained by extruding

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and calendering a lubricated PTFE paste, with subsequent removal of the mineral oil lubricant. The thin metallic coating is easily removed by rubbing at this stage. In the case of noble metals (e.g. 500–1,000 Å thick gold) the coated film is then sintered at about 450°C, under tension to prevent deformation, and quenched in water. The film becomes denser, non-porous, stronger and the metallic coating is firmly bonded to the PTFE surface as a conductive film. (0.1–2.0 ohms per square). In the case of other metals, *e.g.* copper and aluminium, a firmer bond is formed, and oxidation avoided, if the sintering operation after metal deposition is carried out while still under vacuum. Heat is applied by radiation from hot wires. Further amounts of metal may be added by electroplating and conductors may be soldered to the coating. Thick coatings reduce flexibility. Adhesives, varnishes, etc. which are not adherent to PTFE, will adhere to the metal coat. Metal coatings may be removed, by chemical action or electrical discharge, from specific areas to provide printed circuits, condenser elements, test electrodes etc. PTFE films produced by methods other than paste extrusion may be similarly coated, by vacuum deposition and sintering. The method is also suitable for coating of other PTFE shapes of unsintered polymer, or of tetrafluoroethylene copolymers. (See also Abstract No. 84/II).

M. W. Croze, P. L. Hedrick & Minnesota Mining & Manufg. Co. *U.S. Pat.* 2,689,805

84/II

Improved Method of Coating Polytetrafluoroethylene

United States. Previous attempts have been made to obtain firmly adherent metal coatings on the surface of polytetrafluoroethylene. The only known method which has given any success consists of coating the surface of sintered polymer with a mixture of metal particles and unsintered particles of polymer. Upon heating, the resultant metallic coatings are thick and poorly conducting by comparison with the quantity of metal, and the dielectric strength of the polymer is reduced. The method claimed in this invention consists of depositing the metallic film of evaporation in vacuum on to the surface of unsintered polytetrafluoroethylene. Upon sintering the coated material, the metal is found to be firmly bonded, but may be easily removed by chemical etching. The metallic surface is also suitable for bonding to other materials which cannot normally be bonded to the polymer. Two examples of the use of the invention are given. In the first, the method of preparing a ribbon of unsintered polytetrafluoroethylene is described. This is low in tensile strength but self-supporting, it may be placed in a vacuum chamber and the desired metal deposited by evaporation. Gold is a typical example which has been deposited to a thickness of 500–1,000 Å. The coated film is then heated in air to the sintering temperature of 450°C, when it becomes strong and non-porous. The resistivity of the metal coating is found to be 0.1–2 ohms per square. In the second example, the ribbon or film of unsintered material is prepared and vacuum coated but is then sintered under vacuum, not in air. This has the advantage that metals may be deposited which would oxidise should the sintering be carried out in air. Nickel, silver, copper and aluminium are among those which have been successfully applied. The metal coating may be increased in thickness by electroplating. Thin copper films on polytetrafluoroethylene may also be soldered directly. Applications of the above processes include printed circuits and capacitor manufacture. (See also Abstract No.: 83/II).

M. W. Croze, P. L. Hedrick & Minnesota Mining & Manufg. Co. *Brit. Pat.* 756,814

85/II

A Study of the Formvar Replica Process

See Abstract No.: 65/II

86/II

Thermal Degradation of Unvulcanised and Vulcanised Rubber in a Vacuum

United States. The pyrolysis of rubber samples, the composition of which is given in the table below, was

Composition of Rubber Samples

Sample No.	Composition before Vulcanisation and Acetone Extraction. Parts							Vulcanisation Conditions		Acetone Extraction	Combined Sulphur %
	Pale crepe	Sulphur	Zinc Oxide	MBTS	Stearic Acid	PBNA	Carbon Black	Min.	Temp °C		
1	100	—	—	—	—	—	—	—	—	No	0
3	100	2.5	5	—	—	—	—	300	150	Yes	2.0
5	100	2.7	5	1.5	—	—	—	40	140	Yes	2.2
7	100	3.0	5	1.0	3	1	40	40	140	Yes	2.1
9	100	2.5	5	1.5	2	—	40	60	140	Yes	1.6
11	100	—	5	1.5	—	—	—	—	—	No	—

investigated. The apparatus used in earlier work in the pyrolysis of synthetic polyisoprene and purified natural *cis*-and *trans*-polyisoprene was judged unsuitable and a fresh vacuum still was designed. The specimens were placed in a short glass tube after preliminary heating to remove any volatile material. The tube was then inserted into the evacuable glass furnace tube, round which could be placed a Nichrome electric element heated to about 390°C. The fractions volatilised either condensed in the furnace tube outside the region affected by the heater (fraction volatile at the temperature of pyrolysis but not at 25°C, which was designated V_{pyr}) or in a liquid nitrogen cooled trap. This latter fraction was subsequently divided into two parts by further fractionation, a fraction volatile at −80°C but not at −190°C (V_{-80}) and a fraction volatile at 25°C but not at −80°C (V_{25}). The products not condensed in the trap (V_{-190}) were pumped by a small mercury diffusion pump into a sealed volume where they could be sampled and measured. Pyrolysis was complete in 30 minutes and a

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dark brown glassy residue or a black porous residue was left depending on whether carbon black was absent or present in the original sample. The fraction V_{-190} made up less than 0.1% of the original sample and was found by mass spectrometry to be composed of carbon monoxide. The fractions V_{-80} and V_{25} were also analysed by mass spectrometry and V_{-80} was found to consist mainly of isoprene. V_{25} was found to consist of a mixture of terpenes of the general formula $C_{10}H_{16}$, i.e. dimers of isoprene. A Nier type mass spectrometer was used to investigate the larger molecules of V_{pyr} from Sample 1. The larger peaks in the sample corresponded to masses of the formula $C_{5n}H_{8n-1}$ i.e. of ions of multiples of the isoprene monomer, where n varied from 2 to 16. Infra red examination of the original rubber of sample 1 and the fraction V_{pyr}, in the region 2 to 15 μ showed a similarity in the main features of their spectra. The rates of volatilisation were also investigated at several temperatures using the apparatus and technique described by Madorsky, S.S. (*J. Polymer Sci.*, **9**, 133, (1952) and *Ibid*, **11**, 491, (1953)). The reaction rates were not found to be of the first order. The rates are low at first, which is characteristic of polymers that do not contain low molecular weight chains or degradation accelerators. Generally, the rates rose linearly from 5–10% to 42% volatilisation and then fell gradually. The results indicate that rubber No. 3 underwent considerable degradation during volatilisation. Some degradation also occurs during the milling of rubber specimens. The activation energies, set out in the table below, have been calculated from the volatilisation data. They appear to be higher when an accelerator is present. On the basis of these

Rates of Volatilisation

Sample No.	*Temperature, °C*	*Duration of Experiment. Min.*	*Total Volatilised, %*	*Apparent Initial Rate of Volatilisation, % Min.*	*Activation Energy, Kcal./Mole.*
2a	305	380	51	0.120	58
	310	300	51	0.180	
	315	290	60	0.285	
	320	300	71	0.412	
5	310	280	52	0.240	
	315	220	58	0.385	64
	320	150	59	0.606	
9	305	340	54	0.210	
	310	240	55	0.340	64
	315	220	64	0.540	

experimental results, an explanation is offered of the chemical processes involved in the pyrolysis of vulcanised and unvulcanised rubbers. This explains the decrease in size of the fractions −80 and V_{25} and corresponding increase of V_{pyr} when the rubber is vulcanised and also the maximum in the rate of volatilisation curves.

Article by S. Strauss & S. L. Madorsky *Industr. Engng. Chem.* **48**, July 1956 1212-1219

Copper as a High Vacuum Material I.

87/II

Czechoslovakia. The use of copper in high vacuum engineering has increased considerably during the last few years, in particular since highly pure copper such as OFHC copper can be produced on an industrial scale which eliminated the much feared 'hydrogen disease' often exhibited by normal electrolytic copper. Hard-soldering of copper parts in a hydrogen atmosphere is now possible and the use of copper anodes with tungsten-thorium cathodes gives no difficulties. This is one of the explanations why copper which is oxygen free is now an indispensable material in vacuum technology. The author gives a comprehensive survey of the properties of pure copper and its uses in that sphere.

Article by W. Espe *Nachrichtentech.* **6**, Aug. 1956 355-364

Titanium-Carbide-Base Cermets for High-Temperature Service

88/II

See Abstract No.: 204/I

The Stability of Beryllia and Magnesia in Different Atmospheres at High Temperatures

89/II

United Kingdom. Experimental data obtained by various workers on the reactions of beryllia and magnesia have been used in thermodynamic relations to predict and explain the behaviour of the two oxides in water vapour atmospheres, *in vacuo* and in reducing atmospheres at high temperature. Beryllia volatilises rapidly in the presence of water vapour at temperatures above 1,300°C–1,400°C. The loss in weight of a beryllia crucible 10 inch. high, $4\frac{1}{2}$ inch. o.d. and 4 inch. i.d. is calculated to be 50% when fired in air for 2 hours at 1,600°C. Under similar conditions the loss in weight of a beryllia brick $5 \times 5 \times 10$ cm. would be lower, *i.e.* 13.3%, because of its lower surface area/weight ratio. In the firing of beryllia ware airborne beryllia resulting from evaporation may cause a health hazard. The volatility of beryllia is very much lower when it is heated in a reducing atmosphere and it is advantageous to sinter large crucibles in a graphite liner using an induction set. Magnesium oxide is not appreciably volatile in the presence of water vapour until temperatures above 2,000°C have been obtained. Its loss of weight is negligible compared with that of beryllia in water vapour atmospheres. When heated in a reducing atmosphere, however, magnesia losses are so high that a crucible may be lost completely during firing

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at 1,600°C–1,700°C. Magnesia ware should therefore be fired in air or oxygen to prevent loss by decomposition or reduction. Small samples of beryllia heated in a vacuum of about 10^{-5} mm. Hg have shown no appreciable loss up to temperatures above 2,200°C. Calculations and experimental data indicate that, under high vacuum, at 1,600°C BeO(s) vaporises as BeO molecules. Above 2,000°C in a normal vacuum system BeO(s) begins to vaporise by dissociation. Because of its stability *in vacuo* or in reducing atmospheres beryllia should be fabricated and subsequently used as far as possible under these conditions. In the case of magnesia rapid loss in weight has been observed in small specimens at temperatures as low as 1,600°C to 1,700°C under a vacuum of 10^{-4} mm. Hg to 10^{-5} mm. Hg. The behaviour of magnesia *in vacuo* or reducing atmospheres precludes its use at high temperatures in these atmospheres. In the vacuum melting of refractory metals, such as titanium, rapid dissociation of a magnesia crucible would promote violent reaction with the metal, apart from any tendency of reduction by the metal. This may be one factor responsible for the violent reactions and, in some cases, slight explosions reported when magnesia has been used under these conditions.

Article by D. T. Livey & P. Murray *J. Nuclear Energy* **2**, March 1956 202-212

90/II **Vapour Lubrication of Graphite Sliding Contacts**

See Abstract No.: 143/I

91/II **New Waste Paper Recovery Method Developed in Austria**

See Abstract No.: 155/III

28 — APPARATUS COMPONENTS — 28

92/II Article by A. W. Knudsen *Rev. Sci. Instrum.* **27**, March 1956 148-150

Fast-Closing Vacuum Valve

United States. A swinging-gate type valve with associated triggering mechanism is employed as a protective device for quickly stopping a sudden accidental in-rush of air to a vacuum system. The electrical triggering mechanism uses no vacuum tubes. For a large in-rush of air, the valve will close in less than 0.01 sec.

(*Author*)

93/II **Electromagnetically Operated Ultra-High Vacuum Valve**

United States. An all-glass valve suitable for use with ultra-high vacuum is described. It is operated electromagnetically, and is an improvement upon an earlier version which employed a heavy magnetron-type magnet (*J. Appl. Phys.*, **25**, 1954, 1441). The improved operating mechanism enables remote operation of the valve to be used while the vacuum system is being baked. The valve assembly remains essentially similar, *i.e.* a steel slug suspended, *via* an extension rod, from the glass ball of a ball-and-socket joint contained in the vacuum system. The electromagnet is placed round the exterior of the valve just above the level of the slug according to the opening required. The magnet consists of 3 layers (45 turns) of Fibreglass insulated No. 10 wire. Good control could be obtained using a Variac in the primary of a filament transformer capable of delivering 40 A at 5 V. The valve could be maintained open indefinitely, the coil temperature reaching ca. 150°C.

Note by T. P. Vogl & H. D. Evans *Rev. Sci. Instrum.* **27**, Aug. 1956 657

94/II **A Magnetically Operated Vacuum Valve**

United Kingdom. The device described is designed to admit gas at or near atmospheric pressure through a porous plug into a vacuum system. It is rapid in operation, of controllable speed and is entirely free from grease contamination. The porous plug is made from 80 mesh powdered Hysil glass 5 mm. in depth, which is heated gradually in a graphite mould by an eddy current heater until cohesion starts and is then pressed to a final depth of 3 mm. with a slightly convex surface uppermost. The plug is then sealed into the end of a glass tube forming part of the vacuum system. The last few cm. of the glass tube carrying the plug is sealed into the lower end of a wide glass tube held vertically. Mercury is poured into the gap between the inner and outer tubes so that the upper surface of the mercury covers the porous plug surface when a soft iron cylinder of mass 50 g. is floated in the annular gap. This cylinder may be longer than its mean diameter. Gas is admitted through the upper end of the wide glass tube. The leak is opened by passing current through a 500 A-turn solenoid, wound on the outer glass tube so that the iron cylinder is lifted, and the mercury level retreats below the porous plug. With a plug of 2 cm. diameter the rate of flow is such that the pressure of a 150 ml. reservoir, initially atmospheric, is reduced to 1 cm. in 45 sec.

Note by R. M. Claister *J. Sci. Instrum.* **33**, Jan. 1956 34-35

95/II **A Mercury Safety Valve for Electrolysis of Heavy Water**

Pakistan. A design of mercury safety valve maintains a constant pressure in a cell for the electrolysis of heavy water, so minimising the possibility that the electrolyte may be spilled due to sudden changes of pressure across it. The arrangement illustrated is made from Pyrex glass. When exhausted, mercury rises to the barometric

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height in the annular space between two tubes and its level in the mercury bath is adjusted so that it just covers the side joint to the inlet tube. Heavy hydrogen produced by electrolysis bubbles through the mercury against the constant atmospheric pressure whilst oxygen escapes to the atmosphere. As hydrogen has to bubble into a vacuum, it may overshoot and alter the pressure of the cell which would allow air to rush in through the oxygen delivery tube, if it were open to the atmosphere. It is, therefore, dipped into mercury which prevents air entering but allows oxygen to escape.

Note by R. M. Chaudhri *Proc. Phys. Soc.* **68B**, Dec. 1955 1157-1158

A Corrosion Resistant High-Vacuum Valve for Liquids 96/II

See Abstract No.: 15/I

A High Vacuum Tap with Short Outgassing Time 97/II

Holland. The tap described is similar to an ordinary glass stopcock, but in this case the lip of the conical housing is extended into a flange against which a hollow metal cap can be fitted (over the head of the conical plug) and made vacuum tight with an O-ring. A length of flexible bellows sealed into the cap has on its inner end a spring clip which grips the head of the plug so that this may be withdrawn from its seating into the cap. When vacuum is applied, the cap is evacuated and the exposed films of grease on the conical surfaces is rapidly degassed, after which the plug is replaced in its seating. Air is then readmitted to the cap so that it can be removed, leaving the tap ready for normal operation. It is claimed that vacua of the order of 10^{-6} mm. Hg may be reached in about 1 hour instead of several days, and pressure surges on rotating the plug are eliminated.

Note by J. Horseling *Philips Tech. Rev.* **17**, Dec. 1955 184-186

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A Remote Vacuum-Operated Pipette Controller 98/II

See Abstract No.: 156/III

A Liquid Level Regulator for Replenishing Cold Traps 99/II

United Kingdom. For overnight operation of large cold traps, particularly of the conduction-cooled type, it is necessary to keep the coolant level constant by automatic feed from a reservoir flask. In the system described the cold trap is fed through a vacuum-jacketed silvered glass pipe from the reservoir the mouth of which is sealed. The float-type regulator in the trap consists of a cork supported from a pivoted arm. The arm carries a soft rubber disc capable of sealing the end of a metal pipe leading to the reservoir. Where the level in the trap is too low, the disc seals the tube and the build-up of pressure in the reservoir due to evaporation forces liquid oxygen into the cold trap. When the desired level is attained, the cork float raises the disc from its seating and the coolant is no longer fed to the trap. The disc also acts as a safety valve in case the outlet tube should be blocked; a second safety valve is incorporated in the outlet of the reservoir.

Note by H. C. Probyn *J. Sci. Instrum.* **33**, Aug. 1956 322

Metal Gaskets for Demountable Vacuum Systems 100/II

United States. In order to achieve pressures lower than 10^{-6} mm. Hg in a vacuum system, the system has to be baked at about 400°C. The normal rubber O-rings cannot then be used and instead copper gaskets are employed to make the vacuum seals. The author describes two types of 5½-inch. copper gaskets which withstand the bake-out and give leaks smaller than 10^{-6} μ l/sec. The first type consists of a copper O-ring made from 60 mils thick OFHC copper bent into a circle, the ends being electrically welded together in an atmosphere of hydrogen. Annealing is carried out in hydrogen at 950°C. Such a ring (which can only be used once), when compressed between well-machined flanges, gave a leak of 10^{-3} to 10^{-4} μ l/sec. In order to reduce this to less than 10^{-6} μ l/sec. the flanges were subjected to a fairly elaborate polishing procedure which took sixteen hours of working time. Copper oxide deposited on the flanges during baking and the flanges therefore need periodic repolishing. The second type of seal does not require polishing. It consists of a flat OFHC copper gasket of 40 mils thickness, annealed as above. A circular knife edge is machined on to each flange, and these edges penetrate the copper gasket and make the seal. Guide pins are used to line up the knife edges exactly. The gaskets were polished in a lathe but no surface treatment (apart from the removal of burrs) was necessary on the flange in order to achieve the desired vacuum. A few aluminium gaskets were also tried but did not work satisfactorily. The reason for these failures is not understood.

Article by P. J. van Heerden *Rev. Sci. Instrum.* **26**, Dec. 1955 1130-1131

Experience with Metal Foil as High Vacuum Seals 101/II

Germany. Experience with soluble and heat-resistant vacuum-tight flange combinations are described with metal sheets used as sealing foil. The flange design is that used by Paul (*Z. Phys.*, **124**, 1948, 244). A cyclic wedge on the sealing surface of the upper flange fits into a groove of the lower when the two are screwed together. An annular metal foil is placed between the wedge and the groove. This, under pressure of screwing, flows and gives a seal. Flange materials are brass, monel and iron. Flange dimensions, in mm., are given in a table

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reproduced below. Annular sealing foils of ring width of about 1 cm. are employed cut from silver, lead,

Diameter of the Sealing Groove	*Depth of Groove*	*Height of Wedge*	*Thickness of Flange*	*No. of Screws*	*Thread Diameter*
13	0.5	0.8	9–10	2–4	3
23	1.0	1.3	10	4	6
35	1.0	1.3	13	4	6
50	1.0	1.3	13	4	8
63	1.0	1.3	14	4	8
80	1.0	1.3	14	6–8	8
100	1.0	1.3	14	6–8	8
120	1.0	1.3	14	6–8	8

Article by H. Hintenberger Translated by A.E.C. (2554) *Z. Naturforsch.* **6A**, 1951 459-462

aluminium or copper foil. Of these, aluminium, between 0.2 and 0.4 mm. thick, has been found to be the most satisfactory material.

102/II

Mechanically Sealed Beryllium Windows for Permanently Evacuated X-Ray Tubes

United States. Refers to the difficulty of constructing satisfactory windows for x-ray tubes. Tubes were built successfully with windows of aluminium foil, mechanically clamped, but the foil was easily punctured. Beryllium has lower x-ray absorption than Al and can be used much thicker; previously, the difficulty of soldering Be and its tendency to crack on cooling after soldering had been a problem. In the tubes described, the Be window, which may be as thin as 0.25 mm. is clamped with a soft metal gasket to a steel window frame. The frame is actually a flange, copper-brazed to a nickel-iron sleeve, which is sealed to the side of the glass envelope of the tube, and the window and gasket are clamped down by a second steel flange with 12 fixing screws. In other respects the tube is conventional, with fixed anode, and is operated at 5 mA and up to 15 pkV. from a mains transformer without rectifier, Some data are presented on the performance of the tube. Particular attention is drawn to the almost uniform intensity over a range of 15° either side of the central beam, using a $\frac{5}{8}$ inch wide Be window and a 30° target. It is claimed that improved performance in this respect has been obtained with lower production costs. Comparative absorption data for Al and Be are given, showing that at 10 pkV the thickness required to reduce the initial radiation to half value is in the ratio of 48:1 in favour of Be. Figures are also given for cellophane in the low-voltage range, as giving some idea of the absorption in human tissue.

Article by J. T. Perry *Rev. Sci. Instrum.* **27**, Sept. 1956 759-762

103/II

Device to Protect Windows in Vacuum Evaporation Plant

Germany. Persistent trouble is experienced with the coats forming on observation windows fitted to vacuum evaporation apparatus. Remedies suggested in the past, such as the provision of window wipers, have proved ineffective. A novel arrangement is proposed which keeps the windows virtually free from any deposits and which is based on the consideration that vapour particles move at less speed than light. Essentially, the arrangement consists of a cylindrical drum which is fitted inside and in front of the observation window of the plant on an axis parallel to the plane of the window. The axis carries a stationary diaphragm of a given slot dimension and the drum carries a multitude of slots parallel to the axis. At a suitable speed of the rotating drum the vapour entering through any of the slots on the drum will either be stopped on the stationary diaphragm fitted to the axis of the drum or alternatively will deposit on the inner circumference of the solid drum section immediately in front of the observation window at that moment. The following dimensions are suggested in order to achieve good protection: Drum diameter–100 mm., number of slots in the drum–24, slot depth–2 mm. distance slot-slot–11 mm. and speed of the drum–10,000 r.p.m.

R. Koops & C. Zeiss *German Pat. Appl. No.* Z4921VI/48b

104/II

Handling Alpha-Active, Pyrophoric Materials II. Glovebox Design and Construction

United States. In the design of gloveboxes, the size has to be determined so as to balance the conflicting claims of providing (*i*) sufficient space and (*ii*) accessibility so that the operator can reach to any part without the use of tongs etc. Smaller boxes have the advantage of greater rigidity, the shorter welds mean fewer chances of leaks and smaller gas volumes need to be purified when using an inert atmosphere. To achieve these advantages when using large equipment the Argonne National Laboratory developed a flexible design using a strong rigid frame with standardised flanges, bolt locations etc., so that several boxes could be coupled to form an interconnecting system with glove ports in tiers of two or three back and front. The windows in these large gloveboxes were of CR-39, an allyl polymer which has high resistance to scratching and chemical attack. The smaller gloveboxes used in the research laboratory had windows of safety glass which makes the system easier to purge and clean than one using plastic. High vacuum techniques are necessary for joints and gaskets so as to protect against contamination leakage, and to maintain inert atmospheres. Unrestrained flat gaskets are not dependable and standard O-ring gaskets do not lend themselves to the normal rectangular shape of gloveboxes. Very promising results have been obtained with mitred and vulcanised square-cornered O-rings fitted into rectangular milled grooves. Gas-tightness should be ensured during construction without resort to caulking or sealing com-

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pounds. The 'vacuum technique' of applying a thin layer of vacuum grease such as Apiezon to the gasket is recommended for leak-tight joints. Extra openings should be provided, also at the time of construction, for such items as electrical leads, moveable shafts and tubing. The gloves themselves are possibly the most vulnerable part of systems where radio-active and pyrophoric materials are handled. It is preferable to improve glove quality rather than glove changing technique as the latter is always a potential hazard. It has been found that Neoprene gloves last longer when in continuous use than when used intermittently. There is a need for gloves having special properties for particular applications, e.g. impermeability to moisture for protecting inert atmospheres; for handling highly poisonous materials, bacteria etc. For glove changing, an adaptation of the double-clamp technique has been proved satisfactory. An O-ring acts as a temporary seal during the change and an important part of the technique is the proper use of a suitable low-vapour pressure grease (of the Apiezon or silicon type). Surgeons' gloves provide secondary protection against contamination in the event of a damaged Neoprene glove, and extra outer protection is provided when handling sharp or hot objects. When handling plutonium, the box is kept under negative pressure but this has to be limited to about 1½ inch. of water as the gloves tend to stand away from the hands. This can be countered to some extent by a suitable mounting of the gloves. A problem not yet overcome is that of perspiration.

Article by L. R. Kelman, W. D. Wilkinson, A. B. Shuck & R. C. Goertz *Nucleonics* 14, April 1956 65-71

Servo-Controlled Leak for Mass Spectrometer

105/II

United States. The ion current in a mass spectrometer is maintained at a pre-determined constant value to within 1.1% by a servo system which controls the gas sample flow through a variable leak. The servo can recover from a 100% change in the ion current in approximately two minutes when the leak is located 26-inch. from the ion source. The system consists of a variable leak, a leak drive unit, and a detector-amplifier.

(*Authors*)

Report by R. H. Roberts & K. B. Earnshaw *A.E.C. Rep. No.* AECD-3149 January 1955

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Method of the Removal of Air from Kieselguhr and Similar Porous Filter Materials by Vacuum Treatment

106/II

Germany. Kiesilguhr is used to an increasing extent for filtration processes in beer production. Kieselguhr filters should contain no air in order not to affect adversely the quality of the beer. The conventional methods of de-aering the Kieselguhr mixture as used for such processes are not successful as can be proved by a test carried out by the author and described in the patent. In order to remove all residual air tenaciously adhering to the interstices of the mixture it is proposed to place the mixture in a container holding a certain amount of water and to evacuate this container with the filter in it. After keeping the container under vacuum for about 10 minutes all air should have been removed and in order to make certain that the respective cavities in the material are filled with water prior to the use of the filter, the vacuum should be broken and the filter left in the container for a little while.

K. Keller & Enzinger-Union-Werke A.G. *German Pat. Appl.* ES2141Vc/12d

Solvent Removal by Vacuum Evaporation

107/II

United States. The apparatus previously described (*Analyt. Chem.* **24**, 1952, 1686) for imparting a swirling motion to solvents in their evaporation to dryness by vacuum distillation has been modified so as to increase its versatility, ease in use, and compactness. The stirring device comprises an adaptor of which the rod-like upper portion is accommodated in the hole of a rubber stopper attached to the shaft of a variable-speed motor with gear reducer. The adaptor has a short lateral arm, and below this it is jointed to a connector comprising 1 to 10 tubes, each having a Neoprene stopper. The tubes are placed in a water-bath, usually maintained at 40°C by being set on a thermostatically controlled hot plate. A swirling motion can be imparted to the connector and tubes by means of twisted rubber tubing attached at its ends to a metal U. The lateral arm of the adaptor is connected by rubber tubing to a condenser and safety trap cooled by isopropyl-dry ice mixture in a Dewar flask. From this, there is communication through a bulb and by-pass to prevent splashing, and through a potassium hydroxide trap, to the pump. When a water aspirator is used as the source of vacuum, certain modifications to the apparatus can be made. The design of a swirler condenser for evaporation under such conditions is illustrated.

Article by N. S. Radin *Analyt. Chem.* **28**, April 1956 542-543

29 — MISCELLANEOUS APPARATUS — 29

From Sub-Tropic Temperatures to Arctic Cold

108/II

United Kingdom. The high altitude test chamber installed at A. V. Roe & Co. Ltd., Manchester, is used for the testing of personnel exposed to high altitude conditions (*i.e.* low pressures and temperatures) the checking of components for thermal behaviour or changes in optical properties, *e.g.* the transparencies of windows, cockpits, hoods, etc, the performance of electro-hydraulic motors which tend to leak at sub-arctic temperatures, etc. The test chamber is a cylinder 10 ft. in diameter and 29 ft. in length, evacuated by a 10 h.p. rotary pump (to be replaced shortly by two 130 h.p. units), Refrigeration is effected by two 'Arcton-4' twin-cylinder, monobloc compressors driven by 50 and 25 h.p. motors. Rates of climb up to 20,000 ft./min. to 70,000 ft. altitude can be simulated in the chamber, after the installation of the new pumps.

Article by Anon. *Mod. Refrig.* **59**, Feb. 1956 48-51

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109/II

Leak Detection by Vacuum Techniques

See Abstract No.: 20/I

110/II

Leak Detector

United States. The patent describes a leak detector of the mass spectrometer type in which a cold cathode ion source operating on the principle of the Philips ionisation gauge is used. The tracer gas is helium. The use of a cold-cathode ion source eliminates the need for a cold trap as is necessary when conventional hot-wire ion sources are used in mass spectrometer leak detectors. The beam region is maintained at a lower pressure than the ion source by an auxiliary pumping system, thereby avoiding beam scattering. The cold cathode source is connected to the article being tested which is evacuated and sprayed with helium. The ion beam from the source is defined by a slit in the anode of the cold cathode discharge device which, being held at a positive potential, accelerates the ions into the magnetic field which then causes the ions to follow a circular path. The same magnetic field serves for the source. The source, suppression and collecting electrodes are arranged in a circle inside a circular evacuated chamber. At a position approximately 180° from the source slit, the ion beam is intercepted by a grid and baffle plates forming a suppressor, and held at a sufficient positive potential to prevent all but the high energy helium ions from passing through it. At a position approximately 315° from the source slit, is arranged a collector for the collection of helium ions. The magnetic field and accelerating potential are so arranged that the helium ions admitted through the leaking article pass first into the source, where they are ionised, are then accelerated and deflected by the magnetic field, pass through the suppressor grid and are collected at the collector to be registered on some suitable current measuring device. The leak detector provides larger ion currents than those using conventional hot-wire sources, making observation of ion currents more easy.

R. Loevinger, T. A. Chubb, G. W. Monk & U.S. A.E.C. *U.S. Pat.* 2,727,995

111/II

A New Method for the Detection of Very Small Leaks in Pipe Systems

See Abstract No.: 23/I

112/II

The Omegatron as a Leak Detector

United Kingdom. A simple omegatron has been constructed which can be used with a helium probe to detect gas leaks as small as 10^{-14} l.mb/s. Leaks of this order would have an effect on the performance of a small receiving vacuum tube after a shelf life of, say, 10 years. When evacuated at a rate of 10 l./s. the instrument has a sensitivity similar to that of a magnetic sector mass spectrometer, *i.e.* it will detect leaks as small as 10^{-9} l.mb/s. It is, however, cheaper and simpler to construct. It is also a small instrument in which gas from a leak can convienently be allowed to accumulate until a measurable increase of pressure is obtained. If the omegatron-combination has a volume of 300 cm³ and is isolated for an hour a leak of 10^{-14} l.mb/s can be detected. An advantage over other devices using the accumulation technique, *e.g.* the hydrogen gauge and the oxide-cathode oxygen leak detector, is that a stable zero is only required during the measuring period and not throughout the accumulation time. Standard valve processing techniques can be used for outgassing the instrument. The omegatron is a radio-frequency mass spectrometer which yields an ion current proportional to the partial pressure of the gas present in the instrument. The gas molecules are ionised by a fine beam of electrons flowing in and parallel to a uniform magnetic field. An electric current which alternates with a frequency close to the cyclotron resonance frequency of the gas ions is applied at right angles to the magnetic field to accelerate the ions. In this instrument the r.f. field is set up between two flat plates, 12×20 mm., with folded-in ends. Two trapping plates define the interaction space. These are positive to the r.f. plates and prevent the escape of ions and collect electrons formed in the ionisation process. The electron beam is generated by an 0.05 mm. tungsten filament. It enters the interaction space through an 0.5 mm. slit in one of the end plates and passes out through a hole in the second end plate to a collector kept positive to the end plates. A back plate behind the filament, at filament potential, helps to prevent electron scatter. The ion current is collected by a strip of metal close to one of the r.f. plates, and mounted on a lead which connects to an electrometer. The omegatron is encased in a glass envelope and is placed between the poles of a permanent magnet giving a field of about 2,500 G at the centre. The tube with the suspected leak is connected to the omegatron and an ion gauge via a small liquid air trap. These parts are connected through a glass cut-off valve to a mercury diffusion pump with two traps, backed by a mechanical pump. Water vapour and carbon dioxide are removed in the cold traps. The ion gauge serves to check that the total pressure is at a reasonable level for operation of the omegatron. It is possible to keep the total pressure below 10^{-7} mb for several hours with the cut-off closed. After allowing a suitable time for accumulation, a test is made for resonance and the deflection of the electrometer is noted. The omegatron is limited to use with probe-gases of small mass number. Helium appears to be the most suitable gas for small leaks, especially in metal systems. It diffuses through leaks at a high rate and gives a positive indication on the spectrometer. A disadvantage of helium in testing glass apparatus is that it diffuses through the glass. Helium from the atmosphere diffuses through the glass-ware of the omegatron itself and limits the sensitivity to about 10^{-14} l.mb/s.

Article by R. L. Bell *J. Sci. Instrum.* 33, July 1956 269-272

113/II

The Pirani Gauge

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Penning Gauge as Leak Detector

114/II

Yugoslavia. A modified probe gas technique for cold ionisation gauges of any type is described which facilitates simultaneous pressure measurement and leak detection by the aid of the potentiometer method. The method is simple, accurate and reliable over a large pressure range. The gauge used in the experiments described had an anode ring of molybdenum 0.6 cm. long with internal diameter 2 cm., and two stainless steel cathode plates 1.5 cm. in diameter and 2.5 cm. apart. The applied anode voltage was 900 V and the magnetic field strength 400 *G*. The working range was 5×10^{-3} to 5×10^{-6} mm. Hg. The circuit included a galvanometer G (sensitivity 3×10^{-9} A./mm.) in series with the gauge. The potential difference across G was balanced by a cell and variable resistances. Using H_2 and CO_2 as probe gases, changes of pressure of ca. 10^{-8} mm. Hg could be detected. Use of CO_2 caused the discharge current to decrease with time, due probably to formation of carbonate film on the electrodes. Using H_2, leak detection was possible over the working range of the gauge.

Note by M. Varicak *Rev. Sci. Instrum.* **27**, Aug. 1956 655

Beta Gauge for Localised Measurements on Thin Films

115/II

United States. A device is described which allows non-destructive point-by-point thickness measurement of films used as cyclotron targets. The film is mounted on a microscope-type moveable stage over a collimated beta source, a thin-window Geiger tube being fixed above it. The source was prepared by depositing about 5 mC of carrier-free promethium chloride in a circle of about 0.05 inch diameter on a disc of 0.04 inch thick Lucite plastic. The collimator is made of $\frac{7}{8}$ inch thick Lucite with a $\frac{3}{32}$ inch hole through it. surmounted by a $\frac{1}{8}$ inch thick lead washer. The beam is about $\frac{3}{32}$ inch in diameter and thickness variations of less than 0.1 mg./sq. cm. (aluminium equivalent) can be measured for thicknesses up to about 6 mg./sq.cm.

Note by O. U. Anders & W. W. Meinke *Rev. Sci. Instrum.* **27**, June 1956 416-417

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Properties of Evaporated Metal Films Related to Their Use for Surface Temperature Measurements

116/II

United States. The use of evaporated metal films as resistance thermometers for surface temperature measurements is described. The properties of thin films of the most chemically inert and refractory metals have been studied so that stable resistance thermometers can be obtained. With films 300–3,000 Å thick, accuracies of 0.01°C have been obtained for useful periods of time. The advantages of thin films in this application are:—(*i*) Low thermal capacity of the element. (*ii*) Simple resistance measurement (*iii*) Surface topography is unchanged. The useful temperature range is from room temperature up to about 300°C for Co, Cr, Ni and Pt films. The methods of preparation include the use of resistance heated vapour sources and also sources heated by electron bombardment at 4 kV and up to 0.5A. A large number of trial runs were carried out to establish a standard technique of manufacture and use of the films. The mechanical and chemical resistance were compared for different metals by means of abrasion tests and etching tests. In general, the thin films were found to have a greater chemical resistance than the bulk metals. The films were aged artificially by heating at least to the temperature of operation, and this is discussed fully in relation to the method of film preparation. Graphs have been plotted which show the relationship between the resistivity of film and of bulk metal, and the relationship between thickness and temperature coefficient of resistance. The temperature coefficient of thick films can be related to their atomic number. The limitations of thin films as resistance thermometers in various applications have been outlined.

Article by T. B. Simpson & C. C. Winding *A.I.Ch.E. Journal* **2**, March 1956 113-117

A Semi-Conducting Antimony Bolometer

117/II

United Kingdom. Thin films of a semi-conducting form of antimony prepared by sputtering from a cathode of metallic antimony are suitable, with regard to resistivity, temperature coefficient of resistance and freedom from current noise, for the construction of bolometers of good sensitivity and of sufficiently high resistance for matching into a valve amplifier. A description is given of the construction and performance of such a bolometer, in which the antimony film is deposited on a thin plastic pellicle.

(*Author*)

Article by E. J. Gillham *J. Sci. Instrum.* **33**, Sept. 1956 338-341

An Improved Helium Liquefier and Cryostat

118/II

United Kingdom. The rate of production of liquid helium by small scale liquefier-cryostat combinations of the Daunt and Mendelssohn design has hitherto been limited to 4–5 cm³/min. and the maximum volume produced has been 250 cm.³ With such equipment the evaporation loss is low and amounts to 1–2 cm.³/h. The systems are free from contamination and, therefore, the design is very convenient for investigations of the behaviour of helium II. The apparatus here described retains the advantages of the old design but gives a higher output rate and a total volume of 750 cm.³ of liquid helium. The Joule Thomson method of cooling is used as before but the heat interchangers have been redesigned and a metal reservoir has been incorporated inside the evacuated casing to hold liquid hydrogen boiling under reduced vapour pressure. Hydrogen consumption is thereby decreased and the reservoir can be replenished in less than one minute as against 5–10 minutes with the old-type liquifier. By omitting the cooling well at the top of the old-type liquefier, liquid oxygen consumption is reduced and the control knob of the expansion valve never becomes frozen. Precooling of compressed helium to liquid oxygen temperature now takes place outside the main apparatus. Details of the construction and a time table of the liquefaction process are given.

Article by D. F. Brewer & D. O. Edwards *J. Sci. Instrum.* **33**, April 1956 148-150

Multiple Target Nuclear Magnetic Resonance Cryostat

119/II

United States. An apparatus is described for controlling the temperatures to 0.1°K of several solid specimens during nuclear magnetic resonance experiments in the range 10–400°K. The method used is a combination of the 'thermal dam' and vacuum calorimeter. As developed, the apparatus is used to study resonance absorption

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II — Vacuum Apparatus and Auxiliaries — II

Contd.

of high polymers. Details of the design of the apparatus are given. The specimen targets are passed through the r.f. coil of the spectrometer in succession. This procedure enables more certain comparisons to be made of line shapes for different samples. The method is of particular advantage when small changes are to be observed or when it is of importance to have the individual specimens undergo thermal treatments as similar as possible. Also, since several samples can be studied in succession at any desired temperature a considerable saving of time is achieved. The cryostat is designed so that solid or liquid specimens can be utilised with a minimum of disturbance to existing adjustments.

Article by N. Fuschillo *Rev. Sci. Instrum.* **27**, June 1956 394-396

120/II

A Null Method for the Measurement of Low Vapour Pressures

Germany. The determination of the vapour pressures of highly volatile materials can be effected by a variety of established methods, all of them giving reliable values. But the measurement of the vapour pressure of liquid substances, below 1 mm. Hg in normal conditions, is difficult. The authors report on an instrument, developed by them for the purpose. Its operation is independent of the nature of the gases and vapours investigated. The instrument consists of a pressure chamber separated by a thin diaphragm from a compensation chamber. The apparatus is immersed in a thermostatically-controlled bath during measurement. Attached to the diaphragm is a steel pin (diameter 0.021 cm.) projecting into the compensation chamber which transmits any movements of the diaphragm to a small mirror. The movement of the latter can be observed by means of a telescope. The sensitivity of the apparatus is 2×10^{-4} mm. Hg. In operation, both chambers are first evacuated and then isolated. The sample is charged under vacuum into the pressure chamber and kept in constant motion by means of a magnetic stirrer. The vapour pressure of the sample in the pressure chamber governed by the temperature of the bath in which the whole instrument is immersed, will bend the diaphragm outward into the compensation chamber. To compensate for this, small quantities of air, specially cleaned, are led into the compensation chamber until the deflection of the mirror is zero again. Adjustment is complete after 30–60 minutes. The pressure of the air in the compensation chamber is then a measure of the vapour pressure in the pressure chamber and is determined by a McLeod gauge, in the range of 10^{-5} to 10^{-3} mm. Hg, by a thermoelectric manometer in the range 10^{-3} to 10^{-1} mm. Hg, and by a mercury-filled U-manometer in the mm. range.

Article by O. Amsel & G. Wittwer *Z. Angew. Phys.* **8**, Jan. 1956 20-24

121/II

An Investigation of Metal-Ammonia Systems by Means of Their Vapour Pressures

United States. The vapour pressures of calcium-strontium-barium-lithium- and sodium-ammonia systems have been determined as a function of concentration and temperature. The equilibrium pressures of the metal-ammonia system were determined in a vacuum system consisting of a reaction tube, ammonia gas measuring bulb, calibrated standard bulb (each with a mercury manometer) and a liquid ammonia reservoir bulb. The ammonia was twice distilled from a sodium solution before being transferred from the gas measuring bulb to the reaction tube through sintered glass mercury valves. Sodium traps were used to prevent mercury from the manometers reaching the reaction tube. The amount of ammonia in the measuring bulb and reaction tube was calculated from pressure and temperature measurements by means of the van der Waal's equation. For all metals except sodium the metal was weighed prior to an experiment and the amount of metal was also determined by titration following a run. From the vapour curves it was found that the number of moles of ammonia per mole of metal for the solids in equilibrium with the metal for calcium, strontium and barium was 5.67, 4.87 and 7.49, respectively at −63.8° and, in the same order, 5.79, 4.92 and 7.55 at −45.3°. The experiments indicate that the alkaline earth metals do not form the hexammoniate compounds long ascribed to them. A region of two liquid phases was found for solutions of all the metals investigated. It is suggested that the observations are consistent with a non-stoichiometric interstitial type of compound in an expanded metal lattice. The activities of the ammonia and the relative activity coefficients of the metals were calculated for the lithium and sodium solutions and compared with each other and with the corresponding values for potassium and cesium solutions calculated from literature data. The relative lowering of the fugacity was determined for each of the alkali metal solutions and compared with the ideal curves for 1-1 electrolytes and non-electrolytes. The results are interpreted as being inconsistent with the uni-volent electrolytic hypothesis generally given for more dilute solutions.

Article by P. R. Marshall & H. Hunt *J. Phys. Chem.* **60**, June 1956 732-738

122/II

Volatility of Vinyl Plasticisers

See Abstract No.: 152/I

123/II

The Dyeing of Cellulose Acetate with Non-Ionic Dyes III. Dyeing from the Vapour Phase

See Abstract No.: 160/I

124/II

The Production of Transparent Profiles of Dust Particles as an Aid to Automatized Particle Counting

United Kingdom. When using automatic particle counting techniques in conjunction with high power light microscopy for the evaluation of dust particles of sizes below 5 μ, problems arise due to (*i*) the small depth of focus of high power objectives and the close approach to the limit of optical resolution; (*ii*) the commonly poor and sometimes false contrast between the finest particles and the background, and between different parts of single particles; (*iii*) the small quantity of light passed by the objective. Normally, the depth of focus

II — Vacuum Apparatus and Auxiliaries — II
Contd.

Abstract No. and References

is much less than the diameter of many of the dust particles; this involves continual adjustment of the focus setting of the microscope during appraisal of the specimen. An increase in focal depth would be at the expense of resolving power. Many materials in thin section are almost transparent and can behave as miniature lenses giving the appearance of bright centres with dark edges, resulting in multiple counts. The authors report on the use of the evaporation 'shadowing' technique for the solution of some of these problems. Details of the arrangement are given. The evaporating surface was 2.5 mm. in diameter. The distance source-slide was 15 cm. Evaporation was carried out at right angles to the slides. Gold, silver and aluminium were used for the deposits. With all metals the evaporation was carried out at a pressure of about 10^{-4} mm. Hg. The desired attenuation of 90% or more of the incident light was attained with gold, silver and aluminium films of 270, 220 and 120 Å thickness respectively. After the 'shadowing', the particles were most readily removed by a jet of compressed air directed at a very shallow angle to the surface of the slide. After mounting the metal film it can be illuminated by transmitted light in the usual way when the 'particles' appear as bright areas (holes) on a dark ground, or by reflected light when the 'particles' appear dark on a bright ground. The former is preferable for automatic particle counting as the detecting photo-cells are quiescent for the background and give positive pulses when the 'particles' are scanned.

Article by R. J. Hamilton & B. A. Phelps *Brit. J. Appl. Phys.* **7**, May 1956 186-188

Improvements i.o.r.t. Vacuum Pumps 125/II

See Abstract No.: 9/II

Make Own Vacuum Controls 126/II

United States. An automatic control for maintaining a vacuum of about 5 inch. Hg below atmospheric pressure has been developed suitable for use on the steam-heated vacuum drum driers in the Instant Postum manufacturing process. The high sensitivity of the commercially available vacuum controllers was not necessary for regulating this drying operation and a control accurate to 0.2 inch Hg was constructed for about $\frac{1}{10}$ the cost of the commercial units. An ordinary laboratory pipette was sealed on one end and bent in a U-shape. Mercury for use in the pipette was heated to boiling point to drive off entrapped air. The glass tube was then evacuated as completely as possible and the heated mercury was poured in to fill the closed limb of the pipette. A vacuum recorder was already fitted on each drum and the open end of the pipette was connected into the vacuum line to each recorder. A photocell relay was arranged to scan the top of the mercury column in the closed end of the pipette. When the pressure and, hence the mercury level, falls below the required value the photo-relay opens a solenoid-operated valve, admitting atmospheric air until the proper operation pressure is re-established.

Article by Anon. *Food Engng.* **28**, May 1956 5-6

Automatic Vacuum Pan Control 127/II

See Abstract No.: 150/III

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Abstract No. and References

III — Vacuum Processing Techniques — III

30 — EVAPORATION — 30

1/III

The Preparation and Uses of Vacuum Deposited Films

See Abstract No.: 28/I

2/III

Method for the Production of Thin Layers

See Abstract No.: 29/I

3/III

Improvements i.o.r.t. Deposition of Films and Coatings

See Abstract No.: 129/I

4/III

Improvements i.o.r.t. the Formation of Evaporated Deposits of Uniform Thickness

S. Taylor & Electrical & Musical Industries Ltd. *Brit. Pat.* 753,311

United Kingdom. Evaporated deposits of uniform thickness are required for many purposes. As material evaporated under vacuum travels in straight lines, these may be produced by having a point source over the centre of the surface and at greater than a minimum distance from it, or by having two line sources along each side of the surface and projecting beyond either end of the length of the surface. Both these arrangements are impracticable in the case of surfaces which must be coated after they are assembled into an envelope. A source is proposed which is suitable for the latter applications. Two line sources, not long compared with the side of the surface to be coated, are mounted parallel to each other on four pillars placed at the corners of a rectangular opening in a flat metal frame. Each evaporation source with its support pillars and the frame forms a closed electrical loop so that it may be eddy-current heated. The sources are made from long metal troughs, along which the material to be evaporated is placed in graduated amounts to produce a uniform evaporated deposit on the surface. In the case of evaporating antimony trisulphide to form a deposit of photo-conductive material on the target electrode of a television pickup tube, line sources 40 mm. long and 27 mm. apart may be used at a distance of 20 mm. from the surface, Five equally spaced beads of material having weights in the ratios of 4:3:2:3:4 are placed in the troughs with the heaviest beads at the extreme ends. The troughs have sides inclined to one another at 90° and are tilted towards each other at an angle of 30°. The beads are first heated in a neutral atmosphere of nitrogen for instance, until they become fused to the evaporators. The unit is then mounted as a whole inside the envelope and the evaporation troughs heated in turn by bringing up an eddy-current heating coil to one and then the other. The evaporator may be left in place after the completion of the pickup tube as it does not obstruct the electron beam.

5/III

Method and Apparatus for Thermal Evaporation

J. C. Ogle, Jr. Libbey-Owens-Ford Glass Co. *U.S. Pat.* 2,748,026

United States. Dichroic mirrors, beam splitting mirrors and a variety of filters comprise a modern class of optical components which are produced by the deposition of several layers of transparent dielectric materials on to a base, generally of glass. Normally deposition is carried out by vacuum evaporation. Even deposition over a large area can be achieved by using a suitably disposed array of sources which work simultaneously. It is desirable in order to effect time-saving, to be able to evaporate all the layers that a particular base is to receive without the necessity of breaking the original vacuum. Accordingly a technique has been described, where a number of sources can, in turn, be rotated into the correct position for evaporation by means of an external control. There are several disadvantages to this technique. To quote an important one, the movement and jarring of the sources on rotation can result in the loss of some of the material and uncontrollable errors in layer thickness may occur. These difficulties are overcome in a new apparatus in which the sources are fixed and displaced a small distance vertically above each other. The base to be coated is positioned vertically facing the sources and a mechanism is provided whereby it can be lifted or lowered vertically by means of a gear system located outside the vacuum chamber and entering it through a vacuum-tight gland. After each evaporation the base is shifted upwards so that it comes opposite to the next source to be used. Correct location is achieved by having a mechanically linked pointer which indicates the position of the frames on a scale. The sources can be individually activated each having its own pair of wires entering the chamber.

6/III

Device for the Deposition of Layers from an Evaporable Material in Vacuum

H. J. Lemmens, M. J. Jansen & N. V. Philips Gloeilampenfabrieken *German Pat. Appl.* N6323VI/48*b*

Holland. Details are given of an evaporation source to be used in vacuum evaporation and essentially designed to counteract spitting and splashing of the material being evaporated. The crucible consists of a cylindrical container, a few cm. in diameter, divided by a partition into two compartments. The lower compartment contains the heating filament and the upper compartment contains the material to be evaporated. The latter is closed by a porous disc made from sintered metal or ceramics, to allow the vapours to diffuse into the chamber and on to the substrate to be coated. In this arrangement, the substrate, if cooled internally, may be as close as 1 mm. to the (porous) face of the source. The construction material of the source depends on the nature of the material used for coating. The source has been employed with success for the evaporation of aluminium, zinc sulphide, copper, silicon dioxide, silver, cryolite and magnesium fluoride.

III — Vacuum Processing Techniques — III
Contd.

Abstract No. and References

Method of Evaporating Metals by an Intermittent Arc in a Vacuum

See Abstract No.: 31/I

7/III

Evaporation from an Electric Arc in Vacuum

8/III

United Kingdom. The author of this letter suggests that evaporation from an arc discharge between electrodes in vacuum offers certain advantages over conventional methods of film deposition. Contamination by a refractory heater is avoided. The method might also be applied to the evaporation of low vapour pressure metals such as platinum. Several workers have already used the method. In arc application, metal ions released from the negative electrode of the arc are accelerated in an electric field in order to increase their energy. In another method the arc is maintained by vibrating the electrodes, and when the receiver is made positive with respect to the negative electrode, many of the emitted atoms are collected. This is a novel way of maintaining the arc at pressures of the order 10^{-5} mm. Hg, which is normally difficult. An early patent by Edison is quoted in which the use of a continuous or intermittent arc in vacuum is claimed for depositing a metal film on the surface of a phonograph record. It is possible that Edison's apparatus was incapable of an ultimate pressure better than a few microns of mercury, at which pressure there are sufficient gas ions to maintain the arc until the electrodes reached the evaporation temperature. Other known cases of evaporation from a discharge are the arc melting of metals, and the cathodic sputtering of high vapour pressure metals in a glow discharge. There are at least three ways in which vapour may be produced in the arc:—(*i*) Sputtering from the cathode under ion bombardment; (*ii*) thermal evaporation of the cathode and (*iii*) thermal evaporation of the anode. Recent work suggests that field emission currents may play an important part in the above. Further study is required.

Letter by L. Holland, *Nature* 178, 11.8.1956 328

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Evaporation Source of Vacuum Evaporation by Electric Arc

9/III

Japan. Reference is made to the difficulty of making a source which will maintain a high evaporation rate for a long period for continuous coating. Previous types of sources use straight electric heating, which is inefficient especially with materials of high melting point, or h.f. induction heating, which requires more complicated equipment. The author's method uses an electric arc, struck between metal electrodes. The first experiments used an intermittent arc, struck horizontally between two electrodes in the vacuum chamber; one electrode was vibrated at 60 c/s, the other was stationary, but could be advanced or withdrawn manually. For Zn, Al and Cu, 3 mm. diameter rods were used; for Ni, Mo and brass, 0.2 mm. thick plates and for W, a bent wire 0.2 mm. in diameter. The work to be coated was supported about 4 cm. above the arc. The discharge appeared continuous, although it consisted of sparks and arcs alternately as the electrodes touched and separated. A current of up to 12 A d.c. was used, and films of considerable thickness were obtained with Zn, Ni, Mo and W. Difficulty with Cu and Al is attributed to loss of heat by conduction along the electrodes to its supports. Another difficulty was the tendency for a continuous arc to strike from brass screws, etc., on the cathode side. The addition of a capacitor in parallel was tried, but the result was to remove relatively large particles in the spark and the films were very poor. The second series of experiments described was with continuous arcs. An anode of doughnut shape was supported by a glass insulator above the cathode, with a carbon rod protruding downwards through the doughnut to act as auxiliary striking electrode. This could be moved into contact with the cathode to strike the arc, after which it was disconnected from the supply so that the arc transferred to the doughnut anode. A stable arc was obtained for currents of more than 4 A, up to about 15 A (the maximum available) with an arc drop of about 17 V. These figures relate to Zn electrodes; good films were obtained and the thermal efficiency was calculated to be over 60%. With Al electrodes, a stable arc was not obtained, even with an improved d.c. supply giving up to 35 A. The anode was then replaced by a hollow doughnut-shaped vessel of Mo, containing Al. A stable arc was then obtained at 35 A and 22 A, and sufficient heat was generated at the anode to melt the A in about 20 secs., giving a good mirror on a glass plate 12 cm. above the source. The authors state that it is not clear whether the main source of evaporation is the anode or the cathode: Clearly the cathode must evolve vapour for the arc to strike and an experiment in which the anode was not given time to become red-hot confirmed this. On the other hand, weighing showed a larger loss from the (Zn) anode than from the cathode.

Article by S. Nagata, T. Nasu & Y. Tomoda *Japanese Vac. Soc.* 7, April 1956 181-187

Reproduction of Printed Patterns by Vacuum Evaporation

10/III

United States. This patent refers to a new technique for the production of metallic or other films on supporting bases where a predetermined pattern is required. It is claimed that the method is superior to the present masking technique because the latter is tedious and expensive for complicated patterns, is difficult to use where the pattern includes completely cut-out areas and does not produce sharp edges unless great care is taken to ensure that the mask is in perfect contact with the supporting body. The technique described here consists in applying to the supporting body a negative pattern comprising a material which is soluble in a liquid which will not attack the metal, or other material, of which the final pattern is to be formed. For example, a conventional printer's zinc printing plate can be made from a negative drawing of the desired pattern. This plate is then used with printer's ink to produce the negative pattern on the supporting body. The whole surface is then coated, say with aluminium, in a conventional evaporating plant. A layer of silicon monoxide can, if desired, be deposited first to improve adhesion, a further layer of silicon monoxide can be evaporated on top of the metallic coating to render it more resistant to abrasion and corrosion. After removal from the evaporator the surface is treated with a solvent—white gasoline containing 10% of carbon tetrachloride is suitable for printer's ink—which dissolves the negative pattern leaving the desired coating on the supporting body.

E.Kafig *U.S. Pat.* 2,748,031

Abstract No. and References	III — Vacuum Processing Techniques — III Contd.
11/III	**Recent Developments in Vacuum Metal Coating** See Abstract No.: 27/I
12/III P. Alexander, A. S. Baxter M. E. Boston & Continental Can Co. *U.S. Pat.* 2,756,166	**Vacuum Metallising and Apparatus Therefor** *United States.* Tungsten is the material normally used for a heater element on which to evaporate aluminium. However, tungsten is attacked by aluminium and this produces a series of difficulties. These difficulties are claimed to be overcome in heaters built in accordance with the present invention. Among other advantages the new design facilitates a service life of up to three hours, compared with ½ hour in the case of the conventional design, making a maximum increase of 200% in the productive operating time of plant possible. Evaporation takes place from a heater consisting of a carbon base, of suitable shape for direct resistance-heating or indirect induction o relectron bombardment heating, covered with a layer of vanadium or titanium carbide having an excess of the metal in its outer layers. Aluminium wets this outer layer and so evaporation takes place all over the evaporator allowing a lower overall temperature to be maintained. For details also see Abstract No. 14/III. The method of making the heater elements is briefly indicated as follows: Titanium-carbide covered heaters, for instance are prepared by dipping, brushing or spraying a suspension of finely divided titanium hydride in alcohol over the surface of the carbon. A previous heat treatment of the carbon at about 200°C lasting 2 to 5 minutes under a vacuum of better than 1×10^{-1} mm. Hg is required. The coated carbon heaters are then subjected to a temperature of 1,800°C for 1 minute in a vacuum of 1×10^{-3} mm. Hg. Two such hydride coatings and firings are needed to produce a suitable carbide layer. Vanadium-carbide layers may be similarly produced from the corresponding hydride if the firing temperature is reduced to 1,750°C. Dispersions of the metal may also be used in place of the hydrides, but it is difficult to prevent oxidation of these, as the protective hydrogen atmosphere present during the hydride decomposition is then absent. Alternatively, carbon rods may be heated to about 1,800°C in an atmosphere of vanadium or titanium iodide in a closed chamber. If heating is prolonged in these atmospheres the carbide formed decomposes to give a metallic layer.
13/III	**Improvements i.o.r.t. Coating Metals with Composite Metallic Aluminium Compounds** See Abstract No.: 46/IV
14/III P. Alexander, A. S. Baxter & M. E. Boston *Brit. Pat.* 740,072	**Improvements i.o.r.t. the Deposition of Metals** *United Kingdom.* Deposition by thermal evaporation in a vacuum is satisfactory for a number of metals including gold, silver, titanium, zirconium and, most commonly, aluminium. It is usual for the metal to be heated by contact with a refractory heater in the form of a rod or bar or a trough element directly heated by an electric current. The refractory metals employed e.g., tungsten, are attacked by molten aluminium and must be frequently replaced. This disadvantage has never been satisfactorily overcome. The invention described claims to provide a commercially satisfactory heating element in particular, for use with aluminium. The element consists principally of a carbon rod or strip with a coating of a metal carbide with a proportion of free metal e.g. titanium carbide with at least 5% free titanium. The aluminium is fed into the element in the form of wire or strip, and flows over the whole surface to form a thin evaporating film of molten aluminium. The carbide layer is hardly attacked, and the proportion of free metal enhances the flow of aluminium. The carbide layer may be formed by applying to the carbon rod a suspension of metal hydride or nitride, and heating to about 1,800°C. Carbides of metals other than titanium are suitable, e.g., those of Zr, Hf, V, Cb, Ta, Mo and W, but titanium is the most satisfactory. (See also Abstract No. 12/III.)
15/III Report by A. I. Weinstein *A.E.C. Rep.* No. BNL 2229	**A Technique for the Production of Self-Supporting Gold Films** *United States.* A self-supported thin gold film, suitable for alpha-particle absorption measurements, may be produced by the vacuum evaporation method. A uniform film of 1 mg./cm.^{2} is obtained in a form convenient for handling. A thin layer of a polystyrene (0.5 g.) in amyl acetate solution (40 ml.) is spread on a 6 × 6 inch. glass plate, and air-dried to give a polystyrene coating. The plate is centred, coated side down, 7 inch. above a metal evaporator filament. The filament is a slightly curved tungsten ribbon, 3 mil × ⅜ inch × 2½ inch. The coating of gold is made in two runs, the gold charge being a ⅞ × ⅛ inch piece of 10 mil sheet for each run. The filament is fired at 90–100 A, and evaporation is carried out at 0.1 micron Hg. The plate is allowed to cool for 15 mins. before restoring the atmospheric pressure. The edges of the film are then broken and the film stripped in warm water. Finally the film is pulled taut over a frame and dried. Repeated dipping in ethyl acetate removes the polystyrene.
16/III The General Electric Co. Ltd. & K. F. Wiles *Brit. Pat.* 744,002	**Improvements i.o.r.t. the Evaporation of Metallic Films on Articles by Thermal Evaporation** *United Kingdom.* In the normal method of vacuum deposition of metals, the metal to be evaporated is placed on a filament consisting of some refractory metal such as tungsten and enclosed in the vacuum chamber with the surface to be coated. Upon passing a current through the filament the metal placed thereon melts and evaporates, condensing on the substrate as a thin film. Nickel-chromium films have been produced in this way for use as resistance elements, but the alloy is difficulty to evaporate since it forms a low melting point alloy with tungsten. This difficulty has been overcome in the present invention by electroplating the tungsten filament with platinum or rhodium to a thickness of the order 5–50 millionths of an inch. An alloy containing nickel such as 'Nichrome' may be now evaporated readily on to a variety of substrates, including glass, resins, or ceramics.

III — Vacuum Processing Techniques — III
Contd.

Abstract No. and References

Improvements i.o.r.t. The Metallisation of Plastic Materials

17/III

United Kingdom. Vacuum metallisation of flexible plastics has proved difficult because of the high volatility of the plasticisers contained in the plastic resulting in poor adhesion between the plastic and the metal film. To overcome this difficulty it is proposed to coat the flexible plastic (such as cellulose nitrate, cellulose esters and vinyl polymers) with a non-metallic material impervious to the volatile substances in the plastic. This barrier layer, on to which the evaporation of metal takes place, has good adhesion to both the plastic and the metal film. Suitable materials are nylon, zein and gelatine. The latter works most efficiently if a 0.001 inch thick film of unplasticised cellulose nitrate is applied to its surface before metallisation. Details are given of a test to evaluate the adhesion of the metal film. Applying this test it was found that aluminium films deposited on cellulose nitrate material plasticised with 40% by weight castor oil, after a barrier film of nylon approximately 0.3 oz./sq.yd. had been applied using a solution of nylon in alcohol and hot water, gave consistent reading of 100% adhesion.

R. D. Brace, R. W. Maxwell & Imperial Chemical Industries Ltd. *Brit. Pat. No.* 745,819

Improved Method of Coating Polytetrafluoroethylene

18/III

See Abstracts No.: 84/II

Method for the Manufacture of Plastic Articles Having Reflecting Surfaces Thereon

19/III

See Abstract No.: 76/I

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Laminated Thread

20/III

United States. In the past, threads of metallic appearance as employed in embroidering, braiding, knitting, etc. have been provided in the form of a metal foil strip laminated on both sides with transparent strips of cellulosic material. The minimum thickness of the foil available for the purpose is of the order of 10^{-3} mm. When such thread is twisted, its appearance is dull. Further, laminated foil thread of this kind has a low shock strength and unsatisfactory elongation properties. It is proposed to produce thread of metallic appearance by a method which employs vacuum deposition whereby a sheet of cellulose acetate butyrate of an approximate thickness of 0.0016 inch is coated with aluminium by vacuum evaporation to a thickness substantially below 10^{-3} mm. After deposition, a second sheet of the plastics material is pressed on to the coated side of the first sheet, giving a total thickness of 0.0032 inch, suitable adhesive being used to effect firm bonding. Subsequently the sheet is cut in widths of 1/80th of an inch. Due to the good flexibility and improved elongation properties obtained from applying the new process, a thread of substantially lower width can be processed from the strip cut to the dimensions just mentioned. In addition, subsequent processing of the strip leaves the brightness of the strip unimpaired.

K. E. Prindle, G. Lacy & Dobeckmum Co. *U.S. Pat.* 2,714,569

Vaporised Metal on Synthetic Fibres

21/III

Germany. Brief reference is made to a process developed by the Textile Chemical Research Institute, Badenweiler, whereby gold, silver, chromium and aluminium have been successfully evaporated in a high vacuum on to synthetic fibres, forming strongly adhering layers, 1 μ thick. Research is proceeding on rendering the fibres durable and washable. Electrically-conductive metallised Perlon tissues are also being investigated.

Note by Anon. *Prod. Engng.* March 1956 8529-151

Coatings for Vacuum Metallised Plastics

22/III

United States. Vacuum metallising processes are used to give a mirror-like, plated appearance on plastics. Very few plastic materials can be metallised directly because of the presence of mould flaws and surface blemishes and the absence of lustre. Normally a lacquer base coat is required to provide the requisite smooth base for the metallic film. The base coat must have perfect adhesion. Only certain solvents can be used in the material for the base coat to avoid 'crazing' of the specific plastic. The base coat must be capable of being 'cured' so as not to be affected by a subsequent top coat, the 'sandwich coat' of metal being too thin to form any barrier against solvents. 'Curing' is delicate for various reasons, *e.g.* many of the cellulose plastics, and some other, like polystyrene, cannot withstand high temperatures. Finally, the base coat must prevent outgassing of the volatiles in the plastic as this increases the pump-down time in the vacuum chamber. The material for the topcoat (applied for protective purposes) should have very good clarity and flow-out in order to preserve the gloss and brilliance produced by the metallic film, and should also take dyes. Variables such as differences in the plastics themselves, methods of application, methods of production, colours desired and durability requirements have made it impracticable to formulate a 'universal' base and top coating satisfactory under all conditions and coatings are still devised to meet the specific conditions of the job in every case.

Article by C. C. Barbera *Industr. Finish.* February 1956 53-54

Method of Applying Protective Layers to Reflecting Metal Surfaces

23/III

Holland. The provision of reflecting metal surfaces by the deposition *in vacuo* of a thin layer of aluminium or silver on to a base coat of hardened thermo-setting lacquer is well known. In order to ensure durability of the reflecting surfaces various types of protective layer are used. A particularly inexpensive method is described

Abstract No. and References

III — Vacuum Processing Techniques — III
Contd.

which provides a hard, smooth, stable protective layer reducing the reflecting power of the mirror by only a few per cent. According to the new method the protective layer is formed from a thermo-setting lacquer, preferably the same material as that employed for the supporting layer. A suitable lacquer solution consists of a mixture of an ureaformaldehyde condensation product and a non-drying alkyd resin in xylol-butanol. This 'muffling lacquer' may be sprayed on, or distributed by rapid rotation of the component, and is then dried and hardened at a temperature of 15–25°C lower than that at which the base coat was hardened, or even less. This precaution avoids deformation of the metal surface due to reaction of the base lacquer. Hardening of the protective layer is usually accomplished in about 2 hours at 115°C.

C. Korver & Hartford National Bank & Trust Co. *U.S. Pat.* 2,689,802

24/III

Improvements i.o.r.t. Processes for the Production of Thin Flexible Glass Coatings on Wires, Foils and Similar Supports

See Abstract No.: 38/I

25/III

Production of Thin, Flexible Glass Films by Evaporation of Glass in High Vacuum

Germany. In many cases the mechanical properties of glass prevent its application as an insulating material in electrical engineering, *e.g.* it has not hitherto been possible to fulfil the demand for continuous flexible layers of glass. It is well known that very thin layers of glass (less than 10 μ) are flexible but it has not been possible hitherto to fabricate such thin layers, continuously. By vaporisation of glass in a high vacuum and application on metallic supports success has now been achieved.

(*Author*)

Article by W. Haenlein *Congress Intern Verre* July, 1956

26/III

Improvements i.o.r.t. Apparatus for Forming Coatings by Evaporation and Condensation of the Coating Material

United States. Details are given of a coating plant specially designed for the preparation of dichroic mirrors, where it is important that successive coatings of the support are of uniform and accurately controlled thickness in each case. This is achieved by maintaining a constant distance between the surface to be coated and the surface of the evaporating material and this, in turn, is accomplished by contacting the heating element with the material and by advancing the material to be evaporated towards the filament to maintain contact as the material evaporates from the surface of the source. There are two sources, each consisting of a filament fixed permanently in a given plane, and a crucible to take the charge which, as a result of spring action, rises gradually during operation. Both source assemblies are fitted to a turret and by rotation ot the latter each of the two sources may be used in turn for deposition purposes. Immediately above the source in the operational position is a circular metal shield which has a single central aperture, the diameter of which is only slightly greater than that of the heater spiral. In addition, provision is made to mask the source entirely by means of a shutter. The filaments have a diameter of 0.05 inch. If, for instance, zinc sulphide and lead fluoride are to be evaporated, the filament for the former should consist of molybdenum and the filament for the latter of platinum-irridium alloy. The crucibles should be large enough to permit repeated depositions without recharging.

Technicolor Motion Picture Corp. *Brit. Pat. No.* 731,909

27/III

Measurement of the Thickness of Thin Films by Multiple-Beam Interference

See Abstract No.: 108/I

28/III

Measurement of Aluminium Film Thickness

United States. A method is described for the non-destructive thickness measurement of thin metallic films of the order of 500–2,000 Å, *e.g.* the thickness of the coating in an aluminised kinescope. Use is made of the principle that an a.c. carrying coil will lose power to an adjacent conductor. The thickness t of a plane thin film, positioned close and perpendicular to the cylindrical coil is expressed by $t=A(Q_o/Q_1-1)$, where A is a constant, Q_o is the Q of the isolated coil and Q, is the Q in the presence of the film. Electrical design data are given, and operation and calibration are briefly discussed.

Note by C. P. Hadley *Rev. Sci. Instrum.* **27**, March 1956 176

29/III

Improvements i.o.r.t. Coatings for Optical Elements

See Abstract No.: 100/I

30/III

On the Reflection and Transmission of Light Through Thin Transparent Films

See Abstract No.: 98/I

31/III

Energy Absorbed in Solid Thin Layers

See Abstract No.: 95/I

III — Vacuum Processing Techniques — III
Contd.

Abstract No. and References

A New Look at Transparent Conductive Coatings

32/III

United States. The properties and applications of transparent conductive coatings are reviewed. The majority of these coatings are of a semi-conducting metal oxide strongly bonded to a glass substrate. Those discussed here are of stannic oxide and are prepared by spraying, dipping, or direct application in the vapour phase of stannic chloride solution, with various additives, on to the glass substrate. The resistivity of the films is intermediate between that of semi-conductors and metal. Stannic oxide films can be given a positive, negative or even zero temperature coefficient with the correct processing. A transmission of 88% (in the visible) can be obtained from films of up to 50 millimicrons thickness. Films placed in a vacuum decrease sharply in resistance but tend to recover when returned to normal pressures. The thicker the film the higher is the heat reflectance. The various applications of the films include de-icing or de-fogging layers on aeroplane, ship and car windscreens and windows, antistatic coatings and special lighting effects.

Article by S. M. Dodds *Mater. & Meth.* **44**, 1956 108-110

Improvements i.o.r.t. the Production or Transparent Electricity Conductive Films

33/III

See Abstract No.: 74/III

Electrically Conductive Article

34/III

United States. The method of preparing an electrically conductive article suitable, for instance, as a radar plotting screen described here is a development of the method covered by the British Patent No. 682,264. In its original form, the method provided for the deposition of a metal compound film on to the glass surface prior to the deposition of a pure metal layer. Employing the old method, considerable difficulty was experienced in obtaining products of consistent properties where it was desired to have an article with a resistance of over 5,000 ohms per square and vacuum deposition methods were used. The modified method described here provides for a single film to be deposited on the glass plate (not counting the provision of a protective film as the top coat where desired). This layer consists of a mixture of the pure metal and a metallic inorganic dielectric compound where the dielectric compound consists of the metal and at least one of the elements selected from the group consisting of oxygen, sulphur, selenium and tellurium. Suitable metals are gold, silver, aluminium, platinum, rhodium, etc. By a judicious choice of the relative quantities of each substance in the mixture, adhesion, optical properties and conductivity performance of the product can be controlled. The preferred method of deposition is vacuum evaporation. By providing two evaporation sources, it may be possible, for instance, to deposit the metal and the dielectric compound simultaneously. Special manipulation of this technique facilitates also the production of a graded layer on the glass plate, which is of considerable assistance in obtaining the required optical properties. The uses of the new technique are demonstrated in a number of examples. In one instance, two evaporation sources are provided, one loaded with 0.310 g. of gold and the other with 0.040 g. of titanium dioxide. Evaporation was simultaneous. The product showed a reflection value of 16½% on the coated side of the glass plate and 5½% on the uncoated side of the glass plate. Light transmission was 56% and the electrical resistance was 9,000 ohms per square.

W. H. Colbert, W. L. Morgan, A. R. Weinrich & Libbey-Owens-Ford Glass Co. *Brit. Pat.* 757,072

A Study of the Effect of a Bismuth Oxide Support on the Conductivity of Very Thin Films of Certain Metals

35/III

France. Previous workers found that the conductivity of gold films is increased if the film is deposited on a substrate which was previously coated with a bismuth oxide layer. The present authors investigate this phenomenon, explored so far only on comparatively thick films, on thin films of various metals and in a temperature range reaching down to liquid hydrogen temperature. The bismuth oxide layer was sputtered on to a Pyrex glass slide from a bismuth cathode in a 50% oxygen atmosphere. The metal was then evaporated on to the bismuth oxide film at a pressure of 5×10^{-6} mm. Hg. The metal film was then aged by baking at 300°–320°C. In some cases, a top layer of bismuth oxide was deposited in addition. Metals investigated were silver, gold, platinum, copper, aluminium. Generally speaking, the present authors found that the same conditions applied in the case of granular films as in the case of comparatively thick films investigated previously. While the effect is most pronounced with gold and silver, it is almost negligible with platinum, copper and aluminium. In conclusion, it is suggested that epitaxy plays a part in producing the effect in question.

Article by S. S. Minn & S. Offret *C.R. Acad. Sci. Paris* **242**, April 1956 2117-2120

Properties of Selenium Rectifiers in the Presence of Various Impurity Centres

36/III

See Abstract No.: 64/I

Conductivity Changes in Silver Films Charged Electrostatically

37/III

Germany. Reference is made to experiments conducted some twenty years ago on changes observed in the conductivity of metals when charged electrostatically. It was then postulated that the charge effects a change in the number of free electrons which, in turn, results in a change of the conductivity. The author reports on a fresh study of these phenomena conducted with the aim of tracing the cause for the inconsistency of the results obtained in previous work. The present investigation was carried out with evaporated silver films. The methods employed in measuring and recording any observed conductivity changes are described in detail. The author succeeded in proving qualitatively, though not quantitatively, the above postulate. However, he found that the conductivity changes are considerably reduced in the case of aged films and this observation may lead to an explanation of the reasons why the results of previous work were inconsistent.

Article by A. Deubner & K. Ramble *Ann. Phys.* **17**, 1956 317-328

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Abstract No. and References

III — Vacuum Processing Techniques — III

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38/III

The Effect of Incident Atomic Velocity on the Structure of Evaporated Silver Films

See Abstract No.: 131/I

39/III

The Effect of the Substrate on the Crystallisation of Metallic Films

United States. This work was undertaken to discover the importance of substrate structure in determining the crystallisation of thin metal films condensed in vacuum. It has already been shown that surface cracks act as nucleation sites for condensing atoms. Films of gold, silver and zinc were deposited on various alkali halide single crystal surfaces by vacuum evaporation to a thickness of about 25 atomic layers. The crystal structure of the deposited film was viewed under oblique illumination using an optical microscope $\times 140$. Smaller crystallites were just visible at this magnification. Films on water-polished surfaces were found to have a uniform structure of small crystallites, but films on cracked and scratched NaCl and KBr single crystals showed groups of larger crystallites. Scratches were deliberately made with a sapphire stylus and a diamond point, when it was found that rows of large crystallites were formed on each side of the scratch. Similar rows of crystallites were found along a cleavage step. Specimens heated after water-polishing also contained nucleation sites for large crystallites, which were found to occur singly, in clusters, and in rows. Similar films were also deposited on to water-polished surfaces which had been kept for many months, showing that there was possibly a rate of formation of the nucleation sites which could be measured. A quantitative study of the occurrence of crystallite rows was therefore made. Rows of large nucleation sites correspond to defects in the original crystal surface, about which information was required. It was found that the rate of formation of nucleation sites on cleaned polished surfaces varies rapidly with temperature. At room temperature the process takes months but at temperatures above 130°C the process may be complete after 1 hour, when the data are represented by a second equation of the form

$$\frac{n}{n_\infty} = \frac{Kt}{1+Kt}$$

where n and n_∞ are the number of rows per unit area at time t and infinite time, and K is the rate constant. Activation energies of 122 kcal. and 85 kcal. were found for NaCl and KBr respectively. Further experiment showed that site formation was accelerated by x-ray bombardment and by tensile stress. In the discussion, the relationship of the nucleation sites to mosaic boundaries and surface cracks is dealt with.

Article by F. I. Metz & R. A. Lad *J. Phys. Chem.* 60, March 1956 277-280

40/III

An X-Ray Study in High Vacuum of the Structure of Evaporated Copper Films

See Abstract No. 133/I

41/III

The Automatic Recording of Electron Diffraction Patterns Applied to the Study of Evaporated Copper Layers

See Abstract No.: 54/II

42/III

Stress Annealing in Copper Films

See Abstract No.: 134/I

43/III

Filmed Surfaces for Reflecting Optics

See Abstract No.: 99/I

44/III

Multilayer Systems: Antireflecting Systems, High-Reflecting Stacks and Interference Filters

United Kingdom. This paper deals with multilayer optical interference systems which are of importance to scientific photography. The conditions necessary for the extinction of reflected light from a surface are dealt with, and both single and double layer antireflection coatings are discussed. A simple determination of the amplitude of the reflected light in both systems is given using a vector diagram. Because of the difficulties of matching the refractive index of the single dielectric antireflection coating to that of the glass, complete extinction with the single layer is not usually possible, but with the two-layer system this can always be achieved for a particular wavelength at a given angle of incidence. Another type of two-layer system is described which has a lower average reflection over the whole visible spectrum. In some instruments there is the need for a mirror which partly reflects and partly transmits light. Metal films are inefficient because of their absorption. All dielectric non-absorbing layers may be built up to give a very high reflection with little absorption. Quarter-wavelength layers of zinc sulphide and cryolite may be stacked in this way, but are not suitable as reflectors over a wide band, since they are selective. Interference filters of the Fabry-Perot type, consisting of two highly reflecting surfaces separated by a spacing layer are discussed. The passband and band width may be predetermined, and the density gradient may be controlled, thus giving them many advantages over the dye-type of filter where narrow band widths are desired. Filters having very high transmissions and wider band width may be obtained by using the all-dielectric stack already described.

Article by O. S. Heavens *Photogr. Sci.* 4, Jan.-Feb. 1956 21-24

45/III

Broad-Band Multilayer Film for Fabry-Perot Interferometers

See Abstract No.: 105/I

III — Vacuum Processing Techniques — III
Contd.

Abstract No. and References

The Reflecting Multi-Dielectric Layers Applied to the Fabry-Perot Interferometer Theoretical and Experimental Studies of the Real Layers — 46/III

See Abstract No.: 106/I

Method of Producing an Intermediate Metallic Oxide Film in a Multiple Layer Article — 47/III

See Abstract No.: 75/III

Reflection-Reducing Coatings of Magnesium Fluoride and Lithium Fluoride in the Near Infrared — 48/III

United States. Following a treatment due to Straton, expressions are derived for the transmission of flat plates whose thickness is large compared with the wavelength of light, both uncoated and coated with layers of another material of a thickness comparable with that wavelength. The effect of films of magnesium fluoride and lithium fluoride on bases of fused quartz, dense flint glass, magnesium oxide (periclase) and synthetic sapphire (Al_2O_3) have been studied for wavelengths of 2 and 3.6 microns. The former wavelength was chosen as it is in a region of spectral interest and the latter was chosen as an upper limit, as the base materials had an increasing absorption below 4 microns. The film thicknesses were estimated by their reflected colours in visible light. This method was sufficiently accurate as the transmittance maxima are broad. Difficulty was experienced with the thicker coatings of magnesium fluoride pealing from their base. This was probably due to temperature inequalities during vacuum coating. Absorption bands have been noted in the transmission characteristics of the coated samples. These are attributed to water. A discussion of the refractive indices of the materials used is given. Values of the refractive indices calculated from the transmittance of the films are compared with those given in the literature for this region of the infrared. The variation of the refractive index of synthetic sapphire is shown by a graph using data from both sources.

Article by J. R. Jenness, Jr. *J. Opt. Soc. Amer.* **46**, March 1956 157-159

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Improvements i.o.r.t. Bulb Washing and Reflector Coating Apparatus — 49/III

See Abstract No.: 75/I

On the Measurement of Electric Constants of Thin Metallic Films — 50/III

Italy. The present work deals with Hall effect and specific conductivity measurements in the case of a non-uniform current density field (that is, when the specimen is not a parallelepiped but has irregularly waved surfaces). It is then impossible to measure separately R_h (Hall coefficient) and σ (conductivity); it is possible, however, to get their product, the Hall mobility of the carriers. These conclusions are important when dealing with thin films, where the actual geometry of the surface is completely unknown. The preceding remarks are used to interpret the results of some experiments on Au films evaporated on mica. An almost constant mobility is found *versus* mean thickness, but its magnitude is about $\frac{1}{4}$ the bulk mobility. This behaviour raises some question about the structure of thin films, and some connection seems to hold between the experiments here described and the results of the measurements of the optical constants of metals.

(*Authors*)

Article by G. Bonfiglioli & E. Wen *et al.* *J. Appl. Phys.* **27**, March 1956 201-203

Effect of Magnetic Field Strength During Condensation on the Coercivity and Form of Vapour-Deposited Iron — 51/III

See Abstract No.: 132/I

Method of Making Electrical Capacitors — 52/III

United States. This is a continuation-in-part of the Application, now U.S. Pat. No. 2,709,663, quoted in Abstract No. 48/III of Vol. V and describes a procedure of manufacturing electrical capacitors which is essentially a special version of the roll coating method. It facilitates the production of capacitors very much smaller in volume per unit capacity than hitherto obtainable by that method. The conducting film may vary from 100 to 10,000Å and the dielectric thickness may range from 0.03 to 0.3 mil.

D. A. McLean, H. G. Wehe & Bell Telephone Laboratories *U.S. Pat.* 2,754,230

Properties of Evaporated Metal Films Related to Their Use for Surface Temperature Measurements — 53/III

See Abstract No.: 116/II

The Resistivity of Thin Metallic Films — 54/III

United Kingdom. The investigations described were conducted with the aim of comparing the resistivity of antimony and bismuth films measured by direct current and microwave techniques. All observations were made with the specimens removed from the coating chamber. The substrate for each film was a glass cover slip. The pressure before evaporation and the rate of evaporation was the same in all cases. Three films were prepared for each mass of metal evaporated. For direct current measurements the film was deposited between

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electrodes of silver; for microwave measurements, to compensate for the capacitance effect of the glass substrate, an aluminium inductive diaphragm was used at 0.92×10^{10} c/s and at 2.65×10^{10} c/s, an identical cover slip at one quarter wavelength distance away from the specimen. During measurements the power used was low enough to ensure resistivity measurements independent of current. Investigation of the standing-wave pattern on the generator side of the films which were placed at one quarter wavelength from the short-circuit termination gave directly the value of the wave impedance z at the surface of the film. The resistivity could then be calculated from $z=1/\sigma l$, where σ=conductivity of the metal film and l= thickness of film. The thickness of the film was determined by weighing the piece of metal used to prepare the film before evaporation and also weighing the deposit formed after evaporation of about 2 g. of metal. The density of the film was assumed to be that of the metal in bulk. The results for antimony show that there is an initial decrease of resistance with time, probably due to crystallisation of the initially amorphous films, and thereafter a slight increase of resistance after about one hour. The initial decrease was greatest for direct measurement and was less marked the thicker the film. A curve is given showing the relation between resistance and film thickness. In the case of antimony there is no marked difference between resistivities measured by direct current or microwave method. The resistivity of a film greater than 100 Å is greater than that of bulk antimony by a factor of 2.5. The results for bismuth show an increase of resistance with time, greater for direct current measurements, for films less than 45 Å which is attributed to a tendency to form small grains. Thicker films showed constant resistance with time. There is an approximately linear relation between the reciprocal of film resistance, and thickness. The resistivity of the films show that they are greater by factors of 3.6 and 3.0 respectively for direct current and microwave determinations than that for bismuth in bulk.

Article by D. E. Clark *Brit. J. Appl. Phys.* 6, May 1955 158-160

55/III

The Surface Areas of Evaporated Metal Films

United Kingdom. Measurements of the adsorptive capacity of thin films by different workers show different results. This report aims to show the possible causes of these discrepancies. Films of Ni, Fe, Rh, Mo, Ta and W were made by direct evaporation, at two different temperatures of formation (0°C and −183°C). The surface areas of Ni, Fe were measured by the sorption of hydrogen at −183°C, and the remainder by the sorption of oxygen at low pressures. A table, partly reproduced below, shows the results for the above metals, given in

Fast Adsorption at −183°C (Molecules $\times 10^{-18}$/100mg), and Percentage of Atoms Present in Film Surfaces.

System	*Fast adsorption films prepared at 0°C.*	*Fast adsorption films prepared at −183°C.*	*% surface atoms films prepared at 0°C.*	*% surface atoms films prepared at −183°C.*
Ni/H_2	5.0	9.3	1.0	1.8
Mo/O_2	19.5	28.5	6.2	9.1
W/O_2	11.0	14.9	6.7	9.1

terms of the percentage surface atoms. These results have been plotted in a graph showing percentage surface atoms as a function of metal melting point. With the exception of tungsten, these results confirm the theory that the fraction of total evaporated atoms in the surface should increase with the melting point of the metal, because during deposition it is assumed that the low melting point metals would be most mobile. The difference in the results at 0°C and −183°C shows that the sintering of the film by the radiant heat of the filament must also be important. This could account for the observed discrepancies.

Article by B. M. W. Trapnell *Trans. Faraday Soc.* 51, March 1955 368-370

56/III

Chemical Analysis of Thin Films by X-Ray Emission Spectroscopy

See Abstract No.: 157/I

57/III

Semiconductivity and Catalysis in the Nickel Oxide System

See Abstract No.: 156/I

58/III

The Structure and Growth of Oxide Layers Formed on Beryllium

United Kingdom. An electron-diffraction study of oxide layers on beryllium has established that on polycrystalline metal surfaces, at 300°C and over, the oxide developed in a one-degree orientation which varied with the temperature of formation. On abraded beryllium below 700°C, the BeO grew in the (001) orientation, but above 700°C in (100). The oxide formed on smooth, electropolished, coarsely crystalline beryllium at temperatures up to 250°C had a grain-size of about 10 Å, but that formed at 300°C and above measured 60 Å of more, with preferred (001) orientation up to 700°C. Growth of the oxide in air at room temperature was not increased by irradiation with ultra-violet light. On vacuum-deposited beryllium surfaces, the oxide grew epitaxially on the exposed (001) and (110) metal faces, even though at room temperature the grain-size of the oxide crystals was only about 10 Å. This striking case of epitaxy under conditions of extremely limited surface mobility was thus

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observed at a stage only a little beyond that at which the initial nuclei originated from chemisorption. Anodic BeO layers, formed in a nitric-chromic acid solution, grew at a constant rate up to several thousand Å thickness, with a linear current/voltage relationship. The initial very thin BeO layers were amorphous, but on reaching a thickness of 100-150 Å and subsequently, the surface consisted of randomly disposed BeO crystals, 60 Å or more in dia., indicating that in this and similar cases the surface temperature of the growing deposit considerably exceeds 300°C.

(*Authors*)

Article by I. S. Kerr & H. Wilman *J. Inst. Metals* 379-385

The Production of Metallic Colloids

Switzerland. The authors refer to experiments, published previously, see Vol. V, Abstract No. 135/I and give, in the present communication, details of the apparatus employed by them for the production of metallic colloids. Cd, Zn, In, Na and Li have been evaporated on to the suspending medium (liquid paraffin in most cases), the latter being stirred throughout the deposition process. In the case of lithium, concentrations of 25g. in 100 cm³. were obtained, the average dimension of the colloidal particles being appr. 1μ.

59/III Article by J. P. Borel & C. Manus *Helv. Phys. Acta.* 29, 1956 253-254

A Study of the Formvar Replica Process

See Abstract No.: 65/II

60/III

Direct Carbon Replicas from Metal Surfaces

See Abstract No.: 61/II

61/III

A Simple Adaptation of the Carbon Replica Technique for the Examination of Selected Areas in the Electron Microscope

See Abstract No.: 60/II

62/III

Device to Protect Observation Windows in Vacuum Evaporation Plant

See Abstract No. 103/II

63/III

31 — CATHODIC SPUTTERING — 31

The Preparation and Uses of Vacuum Deposited Films

See Abstract No.: 28/I

64/III

Simple, Rapid Sputtering Apparatus

65/III

United States. After a short historical survey giving references to earlier work on sputtering, the authors describe a simple, easily cleaned apparatus made from a 4-inch. Pyrex-pipe reducer sealed by 'O'-rings to two aluminium plates. The larger (base) plate carries a shielded pump line and the work table, and the smaller (top) plate an aluminium cathode support rod and the high voltage connections. A vacuum of between 2 and 3×10^{-2} mm. Hg is maintained in the system, a dry argon bleed being used to maintain the pressure in this range. Currents of 10–20 mA at 3,650V give excellent results. The power supply had poor voltage regulation and this appeared to contribute to a stable operation when small pressure changes occur during operation. The deposition rates in the apparatus of a number of metals are given in a table, partly reproduced below, and experiments

*Deposition rates of Sputtered Metals in Sputtering Chamber.**

Metal	*Deposited Rate*	
	Ångstroms per min.	*μg./sq.cm. of Substrate Area*
Silver	500	52.5
Palladium	270	32.9
Platinum	180	38.5
Nickel	170	15.9
Molybdenum	125	11.3
Ruthenium† (1-inch diam. disc)	45	5.5

* The cathodes consisted of two-inch discs except as noted, the current was 20 mA at 3650 V, pressure was $2\text{–}3 \times 10^{-2}$ mm. of mercury and the atmosphere was residual argon.

† The ruthenium electrodes were furnished through the courtesy of Baker and Company, New Jersey.

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Article by R. B. Belser & W. H. Hicklin *Rev. Sci. Instrum.* **27**, May 1956 293-296

on the adhesion of films to glass, quartz and glazed tile substrates are described. The films produced by sputtering are characterised by high adherence and resistance to structural changes induced by heating. Refractory metals may be sputtered fairly readily whereas their evaporation is difficult or impossible. Uses of the hard, chemically resistant films produced by sputtering these metals are discussed.

66/III

Improvements i.o.r.t. Cathode Sputtering Apparatus

L. A. Holland & W. Edwards & Co. (London) Ltd. *Brit. Pat.* 736,512

United Kingdom. Details are given of a sputtering plant which is designed to facilitate operation at lower than conventional pressures without affecting the distance of cathode to article. Basically the plant consists of a cylindrical chamber positioned vertically on a baseplate and closed by a door at the top end. Baseplate and door form the pole-pieces of an electromagnet. The sputtering cathode is suspended from the door on insulating supports and the baseplate carries an annular cathode surrounding the work holder. In operation the chamber is pumped down to a pressure of 0.08 mm. Hg by conventional means. Then the magnetic field is supplied by energising the magnet and the pressure is further reduced to 3.5×10^{-3} mm. Hg. In the presence of the magnetic field (200 gauss) the electrons travelling on a longer path than in the conventional apparatus are able to produce more effective ionisation of the residual gas and thus enable a cold cathode glow discharge to be sustained at the low pressure mentioned. The anode is connected to the earthed positive terminal of a d.c. supply providing 1,500 volts, the total current being of the order of 150 mA and the current density 0.25 mA sq.cm.

67/III

Controlled Sputtering of Metals by Low-Energy Hg Ions

Article by G. K. Wehner *Phys. Rev.* **102**, 1.5.1956 690-704

United States. Sputtering measurements made using the glow discharges as a source of positive ions are shown to be unreliable. The work reported here was carried out under well controlled conditions by placing the target in a high density plasma of mercury ions sustained by an arc discharge from a pool-type cathode. Measurements of the number of metal atoms sputtered under the impact of one positive ion (yield) were made from platinum in the polycrystalline state. Sputtering from single crystals of metal showed characteristic patterns according to the orientation of the crystal. It was found that atoms were preferentially ejected in directions corresponding to closest packing, *i.e.* along the (110) and (111) crystal planes in the case of face-centred cubic and body-centred cubic crystals respectively. The possibility of ejected atoms being trapped again on the surface is discussed, and micrographs illustrate the re-growth of silver crystallites on a single crystal of silver subjected to ion bombardment. The main part of the work concerns the measurement of the minimum ion energy required for sputtering. The threshold energies of twenty-three different metals are measured under mercury bombardment, at normal incidence. A single relationship was revealed. At threshold energy it was shown that the product of incident ion energy transferred to target atoms and the velocity of sound in the target is proportional to the heat of sublimation of the target metal. Assuming this law, values of threshold energy have been calculated for other gas ions. Experiments were also carried out at oblique incidence, when it was found that the threshold energies were considerably lower. It is concluded that at an ion energy less than 300 eV the fundamental process of sputtering is probably a direct momentum transfer. At higher energies, the process is possibly different, and could better be described in terms of evaporation from locally disturbed regions of the target surface.

68/III

X-Ray Hazard in Sputtering Apparatus

Letter by J. F. Strachan & N. L. Harris *Nature* **178**, 15.9. 1956 588-589

United Kingdom. The authors draw attention to the x-ray hazard arising from sputtering experiments with low-pressure gas discharge tubes or industrial processes involving ion bombardment at ca. 10 kV and above. The need for exercising the precautions of testing and shielding, as for magnetrons, gas-filled and vacuum valves, is stressed. These conclusions were drawn from experiments in which targets of materials, including iron, carbon and uranium, were exposed to the discharge plasma of argon or mercury vapour discharge tubes. Negative potentials of up to 20 kV were applied to the targets, and target currents ranged from 0.1 to 10 mA. Positive ion bombardment at the higher voltages gave rise to copious secondary electron emission. Acceleration of these electrons across the positive ion sheath surrounding the target and collision with the walls of the discharge tube gave rise to the observed x-rays. Fogging of x-ray film at 8 kV and above indicated radiation intensities of ca. 10^{-5} r./sec. six inches from the tube.

69/III

The Deposition of Thin Films of Gold on Cylindrical Specimens by Sputtering

United Kingdom. The sputtering chamber consisted of a cylinder of glass tubing on the inside of which a gold foil cathode was held by washers and bolts. Each end of the glass tube was closed by disc-shaped aluminium or steel anodes. The ultimate object was to deposit thin films of gold on cadmium single crystals but in the preliminary experiments 1 mm. diameter polycrystalline cadmium wire was used. This was supported along the axis of the discharge tube and was insulated from the anodes by small glass insulators. Thus, the actual discharge took place between the anodes and cathode only and excessive heating of the wire was avoided. Before sputtering, the vacuum system was outgassed at 0.1 μ for an hour. Sputtering was carried out in dry air admitted *via* a needle valve after passing through a solid carbon dioxide trap to remove water vapour. The pressure was kept as low as possible (10 μ) consistent with the maintenance of the discharge, in order to obtain the maximum sputtering rate and the sputtering voltage was kept to the lowest possible value (350 volts) to minimise heating of the wire. It was found that for times of sputtering between two and thirty minutes, the gold films showed interference colours. Their appearance indicated that the circular symmetry was excellent and the longitudinal

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symmetry was very good, except near the ends of the wire where the film was thinner. Experiments using chambers of different lengths and diameters showed that the length of wire uniformly covered increased linearly with the length of the gold cathode but was independent of the chamber diameter. A greater rate of sputtering was obtained in a chamber of 1½ inch. diameter than in one of 3 inch. diameter; this is in agreement with the formula due to Townes. The maximum temperature attained by the wire was estimated to be 65°C.

Article by F. R. Lipsett *Brit. J. Appl. Phys.* 6, Dec. 1955 442-444

Study of the Optical Constants of Thin Gold Films

See Abstract No.: 96/I

70/III

A Study of Transparent Highly Conducting Gold Films

See Abstract No.: 97/I

71/III

The Influence of Cathodic Sputtering in High-Vacuum on the Rectifying Properties of Germanium

See Abstract No.: 63/I

72/III

Study of the Effect of a Bismuth Oxide Support on the Conductivity of Very Thin Films of Certain Metals

See Abstract No.: 35/III

73/III

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Improvement for the Production of Transparent Electrically Conductive Films

74/III

United Kingdom. A method is described for the satisfactory preparation of transparent electrically conductive films of gold on glass employing the cathodic sputtering method in preference to vacuum evaporation. Essentially the method consists of applying to the glass plate a thin transparent layer of an oxide of material selected from the group of cadmium, lead, tellurium, antimony and bismuth. Subsequently, a film of gold thin enough to be transparent is deposited in an inert atmosphere free of oxygen. Finally, the compound deposit is subjected to heat treatment at a temperature not exceeding 250°C for a time sufficient to improve the electrical conductivity properties of the film. In some instances a top layer of an oxide is provided and all three layers are deposited by cathodic sputtering. The oxides of the materials mentioned are known to be comparatively easily reduced under the conditions obtaining in cathodic sputtering but, during the deposition of the gold film, there is probably only a reduction of the surface molecules of the oxide layers and the effect is to facilitate the formation of a continuous film of metal. The results obtainable by the use of the method are given in a specific example as follows: A triple layer deposit consisting of an intermediate layer of bismuth oxide 400 Å thick, a gold film 140 Å thick and a top layer of bismuth oxide 400 Å thick, gave an optical transmission of about 82% and a resistance between 7 and 8 ohms per square.

J. S. Preston, E. J. Gillham & National Research Development Corp. *Brit. Pat.* 757,782

Method of Producing an Intermediate Metallic Oxide Film in a Multiple Layer Article

75/III

United States. To prepare multiple-layer coatings on a support in the manufacture of mirrors, low-reflection layers, filters and electrically conducting articles an intermediate film of metallic oxide is often required. This intermediate film may be initially vacuum deposited magnesium, tin, lead, iron or titanium, where the thermal evaporation process is preferred to sputtering because thickness control is easier. On this film is deposited a top coating of a material which is pervious to oxygen at elevated temperatures but which is not easily oxidised. The article is then heated in air or an oxygen-containing atmosphere to 150° to 1,200°F so that the oxidising gas penetrates the top film and oxidises the intermediate metal film. The temperature and time of heating are decided by the nature and thickness of the initially deposited intermediate metal film so that this film is substantially completely oxidised throughout its depth. Suitably pervious and non-oxidisable top layer materials are the metals platinum, palladium, rhodium, iridium, silver or gold; in addition, the non-metallic materials which may be applied are metallic fluorides, silico or silicates such as zircon, or a fully oxidised metallic oxide film such as zirconium oxide or zinc oxide. The following specific examples are given:— (1) A silver mirror article. The intermediate, readily oxidisable film is tin and the coating film is silver. Tin oxide is formed by heating for one hour in air at 700°F. Light transmission and reflection data are given. (2) The intermediate oxidisable film is lead deposited by thermal evaporation and the top film is sputtered platinum. Lead oxide is formed in 1.5 hours by heating in air to 400°F. Optical properties are given. (3) The intermediate film is magnesium and the top coating is magnesium fluoride. The oxide is formed at 840°F in air in 30 mins. A low-reflection article is formed. (4) Readily oxidisable lead is first deposited on glass; on this is deposited a film of gold and then an outer coating of lead. The lead films are oxidised by heating in air for 30 mins. at 400°F. The product is an electrically conducting transparent coated glass. (5) Four films on glass. The first is readily oxidisable, the second is gold, for example, the third is readily oxidisable and the outer film is silica. The effect of the oxidation of the intermediate film may be to increase the bonding action, or to increase the light transmission of the film, or both.

A. R. Weinrich & Libbey-Owens-Ford Glass Co. *Brit. Pat.* 757,897

A Semi-conducting Antimony Bolometer

See Abstract No.: 117/II

76/III

Abstract No. and References

III — Vacuum Processing Techniques — III

Contd.

36 — DRYING — 36

77/III

Automatic Vacuum Pan Control

See Abstract No.: 150/III

78/III

Laboratory Drying Ovens

United Kingdom. A comprehensive specification for laboratory drying ovens is given. Heating is most suitably carried out electrically and glass fibre, asbestos or cork lagging is used to avoid power wastage. The interior of the oven should withstand repeated heating and cooling without deterioration and be resistant to humid atmospheres. Though there is no universal solution to the problem of air flow over the material being dried, a forced circulation is preferable to one relying upon convection. Some form of temperature control is almost always needed and to effect this satisfactorily the thermostatic sensing element should be as near as possible to the material dried and should have a small differential. Overshoot of the heating system is reduced in some ovens by fitting multiheat switches or energy regulators to reduce the power to the heaters once operational temperatures are achieved. British Standard 2648:1955 has been drawn up at the request of the dairying industry for drying ovens used for the determination of moisture by drying in the range 95–110°C, but this standard covers such a restricted field that in most cases the design of an oven for any particular purpose must be the subject of agreement between manufacturer and user. Brief notes are given on the design of tray dryers cylinder dryers, vacuum ovens and infrared ovens, and short descriptions of specialised units for drying tobacco, agricultural samples, paper and woodpulp, coal and chromatography papers.

Article by K. A. Galloway *Lab. Practice* 5, July 1956 269-271

79/III

How to Build and Use Glass Evaporation Plant

United Kingdom. While glass has a thermal conductivity three hundred times less than copper, copper is only two and a half times more efficient than glass when used as a heat exchange membrane. Glass is fragile and this has deterred some people from using it on a large scale. However, because of its fragility, it is automatically handled more carefully. The chemical resistance, resistance to thermal gradients and ease of cleaning of the borosilicate glasses now available make them very attractive materials for large scale processing as well as for pilot plants. The author has constructed a climbing film and a recirculating calandria evaporator in Pyrex glass. These were set up on frames $3 \times 3 \times 14$ ft. high and $5 \times 3 \times 12$ ft. high respectively, made from galvanised tubing held together with Kee clamps. The climbing film calandria was a tube 1 inch in diameter and 10 ft. long enclosed in a 2 inch. diameter jacket. Steam passed through the jacket from the top to a condensed water outlet at the bottom. An entrained liquid separator, consisting of a 5-litre flask with a tangential side entry and top and bottom outlets for vapour and liquid, was fitted at the top of the calandria. The liquid drained into a measuring bulb and thence could be returned to the base of the calandria. The vapour passed through a 25 sq.ft. water cooled condenser to a 6-litre graduated liquid receiver. A vacuum pump was attached to this receiver. First a $\frac{1}{4}$ h.p. rotary pump was used to extract condensable gases and maintain a vacuum of 26 inch. Later a Duplex steam driven boiler feed pump was modified to work as a wet vacuum pump drawing 25–26$\frac{1}{2}$ inch. vacuum and, finally, a high speed vacuum pump was used to create 29$\frac{1}{2}$ inch. when this was required. The condenser used was sufficient to maintain a vacuum of up to 28$\frac{1}{2}$ inch., but above this figure water was drawn into the pump. The condensate could be removed from the receiver *via* a bulb forming a vacuum lock. Both evaporated milk at 5–1 concentration and sweetened condensed milk with 75% solids could be handled in the evaporator. However, at high viscosities, a scale forms on the calandria tube, building up from the lowest point, which reduced the evaporation rate. This latter varied from 0.5 to 0.85 ml. water/sq.cm. depending on the vacuum maintained and the viscosity of the liquid. Similar details are given of the recirculating calandria evaporator.

Article by R. Scott *Food Manuf.* July 1956 291-294

80/III

A Laboratory Climbing Film Evaporator

United Kingdom. The apparatus described was designed for the concentration of heat-sensitive materials in aqueous solution which tended to froth violently when heated under vacuum. The usual type of film evaporator using a single liquid vapour separator was unsatisfactory due to losses of material by frothing. In the design adopted, wholly built from a stock of standard Quickfit parts the working solution is first drawn into a 1-litre separating funnel and then passes *via* a tap to a Liebig condenser used as a preheater. It then flows upwards through evaporating tubes placed in parallel inside a heater jacket consisting of a glass tube 1$\frac{1}{2}$ inch. in diameter with rubber bungs fitted to each end to carry the evaporating tubes. From these the vapour and froth passes upwards to a two-litre cyclone separator and the separator output is led to a spray trap. Vapour passes from the trap vertically down through a series of condensers but any spray collected is returned from the trap to the separator *via* a side tube. The condenser system leads down to two 1-litre separating funnels and can be collected below or re-cycled through the system if required. Continuous operation is achieved by using double condensate and product receivers. The required 10W. pressure in the evaporator is obtained by a water jet pump connected to the separator output line. The intake of dilute fluid is controlled by a valve between the preheater and the evaporator and this valve is adjusted so as to give true climbing conditions in the tube. Evaporation rate is 5.0 litre/hr. at 50°C with a pump pressure of 20 mm. Hg.

Article by P. O. Dennis & H. Shipp *Chem. & Industr.* No. 7 18.2.1956 131-132

81/III

Drying Transformers

See Abstract No.: 79/I

III — Vacuum Processing Techniques — III

Contd.

Abstract No. and References

Field Vacuum Drying of Large Power Transformers Saves Time and Money

82/III

United States. The vacuum drying of large power transformers in their own tanks is a cheap and convenient method for field and repair workshop use. Hot air is first circulated through the transformer to warm it. Minimum requirements of 15 cu.ft./min. of air and 3.4 BTU/min. of heat are needed for each square foot of tank surface. The air should enter the tank at a temperature not exceeding 120°C, if the insulation is dry, or 110°C for oil soaked insulation. Electric heating elements must not be run at temperatures above 150°C to avoid accidental oil vapour ignition. A typical procedure is to heat the transformer until the insulation resistance is constant for four consecutive two-hourly measurements, then the tank is sealed and evacuated to a pressure below 10 mm. Hg. Evacuation is prolonged until four similar insulation resistance measurements again give the same values. Specimen heating and evacuation times are 40–50 and 42 hours respectively. Oil is allowed to enter the tank while it is still being evacuated so that the insulation is satisfactorily impregnated. A slow rate of feed ensures that the oil is degassed and dried before it collects in the bottom of the tank. Oil is added to a level several inch. above that actually required to allow for the drop in level when the vacuum is broken. It is preferable to add dry nitrogen to fill the dead space above the oil, as the admission of moist atmospheric air may cause condensation in the tank.

Article by P. Evans, Jr. *Electrical World* 30.4.1956 82-84

An Improved Method for Dehydrating Meat

83/III

United Kingdom. New developments regarding the vacuum contact plate drying process are reported. In its original form the process yielded a product suffering from slow reconstitution, suitable for wet cooking only, and having a poor texture. It has been found that improvements could be effected by freezing the meat and subliming away the ice, as in freeze drying. The product, after comparatively rapid reconstitution, is almost indistinguishable from fresh meat. Details of the modified method are given.

Article by E. J. Rolfe *Food* June 1956 199-205

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Irradiation and Antibiotics May Team Up to Preserve Meat

84/III

See Abstract No.: 148/III

Better Grapefruit Products

85/III

United Kingdom. Some current American techniques in treating citrus fruits are briefly described. Quick frozen juices are now prepared from grapefruit, tangerines and limes by slight modifications of methods used for oranges. A tendency for concentrates to clarify and form gels is prevented by preliminary heat treatment. Frozen sections of grapefruit are prepared by a process that includes evacuating the tins containing the sections before freezing. The third process described is the preparation of concentrated crystals of orange or grapefruit. These are 2.5 times lighter than quick-frozen concentrate and 8.5 times lighter than tinned whole juice; 96% of the vitamin C content is preserved and the product will withstand a temperature of 100°F for months. The process includes continuous dehydrating of fresh juice, with controlled application of heat and a limited time under vacuum. Essential oils and flavours which escape are trapped in a solid absorbent, which is then powered and added to the crystals.

Article by H. Fox *Food Manuf.* August 1956 338-339

37 — METALLURGICAL PROCESSES — 37

New Horizons in Foundry Progress

86/III

See Abstract No.: 181/I

The Present State of the Industrial Vacuum Melting Processes

87/III

Leichtenstein. The effects which may be achieved by vacuum treatment of metal melts are discussed and the present fields of application are described. The paper treats the methods of vacuum melting applied at present as well as the technical and economic possibilities offered by these methods.

(*Author*)

Article by O. Winkler *Z. Metallkde.* 47, March 1956 133-144

Vacuum Melting Furnaces—An Interim Report

88/III

United States. An historical survey is given of the development of vacuum melting furnaces, in particular in the U.S.A. The essential purpose of vacuum melting is to produce 'clean metal' which in terms of modern technology is interpreted as a metal which is substantially free from all unwanted compounds and has substantially the exact analysis desired. Early furnaces were of the induction-heated crucible type with a capacity not exceeding 5 pounds (1920). In the 1930's furnaces of this kind were built with a capacity of 300 pounds of steel. Intensified developments during the war led to the building of proper industrial types, the first 1,000-pound unit being built by the Universal Cyclops Steel Corporation, jointly with F. J. Stokes Machine Company and Ajax Electrothermic Corporation. The author proceeds to discuss the merits of vacuum degassing and finally gives a des-

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III — Vacuum Processing Techniques — III

Contd.

Article by F. Chesnut *Metal Progr.* November 1955 118-123

cription of modern vacuum arc furnaces which have the decisive advantage of avoiding the necessity for a crucible to hold the metal which invariably tends to liberate gases into the melt. Details are given of modern arc furnaces as employed by the Climax Molybdenum Company which facilitates the production of a four foot long 9 inch round, 1,000 pound ingot of molybdenum every 90 minutes. The melting rate is 12 pounds per minute, the power is 360 kW at 60 V a.c. and the operational pressure is 2 micron Hg. Similar details are given of titanium furnaces.

89/III

P. J. Clough J. H. Moore & Nat. Research Corp. *U.S. Pat.* 2,757,219

Production of Metals

United States. A method of producing rammed liner crucibles for induction-type vacuum furnaces is described. A lining of cement is plastered to the inside of the induction coil and air-dried. Refractory material, preferably magnesium oxide, is then added to form the base of the liner. A mild steel shell of the shape required in the completed liner is supported centrally on this base, and additional refractory material is then rammed in between the cement and the shell. The latter is shored up from its inner side during the ramming operation to prevent collapse or deformation. The magnesium oxide should reach to a height above the level attained by the melt during actual melting operations and the remainder of the space to the top of the crucible may be filled with a refractory mixture of magnesium oxide and sodium silicate. A feature of the patent is that a thin layer of aluminium or an alumium-silicon mixture is used to coat either the entire steel shell or the surface of the shell adjacent to the liner. As a result, water vapour expelled from the refractory during subsequent drying and sintering cannot react with the shell to form iron oxides which would become included in the refractory lining and impair its resistance to molten metal. The coating is preferably sprayed on to the shell in molten alloy form using a molten metal spray gun. The shell may be perforated to facilitate the removal of vapours during drying. Air drying and sintering of the crucible are preferably combined in one process. A charge of metal reactants is placed within the steel shell and heated in an open vacuum furnace to a temperature at which the charge shows the first signs of melting. Heating is continued at this temperature until the refractory is dry. Sintering is then effected by subjecting the unit to vacuum and performing a regular melting and casting run during which the aluminium-coated steel shell melts and becomes part of the charge. Shells consisting of the metal to be processed in the crucible may also be used coated in the manner described.

90/III

Article by H. Forestier & A. Mangin *Bull. Soc. Chim. France* Aug.-Sept. 1956 1200-1202

High Temperature Laboratory Furnace

France. A laboratory-type furnace is described which can be operated evacuated or with an inert or reducing gas filling. The highest vacuum is 10^{-4} mm. Hg and the highest temperature is 2,300°C. It is fitted with a resistance heater consisting of 4 bent tungsten sheets, arranged to give a cylindrical working space, connected to a low voltage supply. The use of molybdenum radiation shields eliminate the need for refractories, reduce gas evolution and restrict thermal inertia of the furnace.

91/III

E. Swainson & Imperial Chemical Industries Ltd. *Brit. Pat.* 720,613

Improvements i.o.r.t. the Melting and Casting of High Melting Point Metals or Alloys

United Kingdom. In order to obtain a homogeneous fully melted ingot or casting in the conventional arc melting furnace employing a cooled crucible it is proposed to provide a centrally disposed orifice in the base of the latter communicating with the (separable) mould. This orifice is kept closed during the initial stages of the melting operation by means of a plate of the same composition as the metal to be melted. When the pool of molten metal forming in the crucible is sufficiently large to form the casting, the plate is melted at least in part, to permit the molten charge to flow into the mould where it solidifies.

92/III

Universal Castings Corp. *Brit. Pat.* 749,546

Improvements i.o.r.t. Casting Apparatus and Method of Using the Same

United States. The reject rate on precision castings made by conventional techniques can be as high as 70%. The principal cause of this wastage can be traced to the interaction of the air present within the mould and the liquid metal entering it. It is proposed to prevent such interaction by evacuating the mould. Air within a mould causes trouble in several ways. Where castings including thin-walled sections have to be made, the liquid metal has to be at an exceptionally high temperature in order to achieve high fluidity. Aluminium, for example, has normally to be raised to 1,600°F whereas the use of an evacuated mould lowers the working temperature to 1,375°F. The higher temperature increases gas occlusion and oxidation, and the resulting castings are porous and therefore have a poor tensile strength. Air is never completely removed from the remote portions of conventionally made castings and thin walls and edges are therefore not accurately formed. Lastly the presence of the air and the associated slow filling time involves the loss of up to two thirds of the material in runners, etc. In the technique described in the patent the mould is porous and can be made of a mixture of 70% calcium sulphate, 27% magnesium silicate and 3% Terra Alba and sugar. The two halves of the mould are clamped together between two pressure plates situated above and below the mould. Either or both of these plates have a pattern of interconnected passages on the face touching the mould. These passages are connected to a vacuum pump. Breakage at the sides is eliminated using knife edges which bite into the material of the mould. Evacuation of the mould cavity is achieved through the porous walls of the mould, the spone opening being blocked by the entry of the liquid metal. This may be poured in from above, or sucked in from below, the latter technique minimises turbulence in the melt. Castings with superior physical properties have been made by this technique, including some with extremely thin-walled sections made under production conditions to a specification accuracy of 0.005 of an inch. The patent includes illustrations and photomicrograph reproductions of two forms of impeller made conventionally and according to the invention. Both impellers are so complicated that it is practically impossible for subsequent metal removal by machining. The porosity of the conventionally made casting contrasts strongly with the homogeneous nature of the impeller cast using the vacuum technique.

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Contd.

Abstract No. and References

Applications of Radio-Active Materials to the Problem of Metals of Very High Purity — 93/III

See Abstract No.: 224/I

Metals of High Purity — 94/III

See Abstract No.: 46/I

Zone Melting Apparatus for Production of High Purity Materials — 95/III

United States. An automatic zone melting apparatus constructed at the National Bureau of Standards is described. It consists of a 'Vycor' tube containing a fused silica or carbon boat holding the material to be purified. The tube is either evacuated or filled with an inert gas. A water-cooled induction coil, supplied from a 5 kW unit, is mounted concentric with the tube on a carriage which is driven along by a $\frac{1}{10}$ h.p. operating on a lead screw *via* a friction clutch. Adjustable stops determine the length of travel; the carriage is then rapidly returned to its original position automatically by the action of a switch which energises a $\frac{1}{10}$ h.p. motor directly coupled to one end of the lead screw. The auxiliary motor is de-energised when the carriage has reached its original position and the cycle of operations is then repeated. The apparatus is being used to produce a series of inter-metallic compounds found between the metal antimony and the metals indium, gallium and aluminium.

Note by Anon. *Engineer* **201**, 10.2.1956 209

Floating Zone Melting of Solids by Electron Bombardment — 96/III

United Kingdom. A method of melting a floating zone in a vertically suspended rod is described. The solid rod is held in chucks in a continuously evacuated enclosure and electrons from a heated, pure tungsten loop filament are accelerated towards the rod by a few kilovolts; the potential of a pair of focusing shields enables the width of the zone to be controlled. The molten zone may be made to traverse the length of the rod by relative motion between the rod and filament assembly. The required power consumption is less than 1 kW. The floating zone technique enables purification to be obtained, without risk of contamination from a crucible, by repeated traversal of the specimen by the molten zone. Moreover, this process frequently leads to the growth of large single crystals. The particular heating method used here has the advantage of simplicity and also permits the method to be extended to many refractory materials, Contamination by evaporated tungsten can be made negligible by using a relatively low filament temperature or by placing the filament so that it subtends a small angle at the specimen. In some cases, a filament of the same metal as that of the specimen itself may be substituted for tungsten.

Letter by M. Davis, A. Calverley & R. F. Lever *J. Appl. Phys.* **27**, Feb. 1956 195-196

The Preparation and Properties of High-Purity Iron — 97/III

See Abstract No.: 218/I

The Bochumer Verein Vacuum Casting Process — 98/III

See Abstract No.: 45/I

Vacuum-Melted Antifriction Bearing Steels — 99/III

United States. Inclusions in steel reduce the life of bearings. Steels rated as inclusion-free have a life of 100–200% longer than average steels. Vacuum-melted bearing steels have stood up to endurance-testing at 130°F twice as well as standard electric furnace steel. At 400°F, vacuum-melted material of 1% V, 0.65% C, 5% Cr and 5% Mo had an average test life of 1,080 hrs. compared with 150 hrs. maximum for air-melted steel.

Note by Anon. *Foundry Trade* 20.10.1955

Controlled-Atmosphere Melting of Magnetic Materials — 100/III

United States. A review is made of the basic equipment required to perform quality controlled-atmosphere melting. The equipment described includes a tightly sealed furnace chamber, power source, vacuum pumping system, and gas purification system. A detailed step-by-step melting procedure is given using this equipment. Careful consideration which must be made in the choice of melting crucible and mould wash for different alloys, including two very successful mould wash mixtures, are presented in detail. Furnace charges and the compositions of the final resulting alloys, for six representative melts, are given. These data indicate the close composition control and minimum of carbon and gases (H_2, O_2, N_2) present in these magnetic alloys. The static magnetic results of commercial alloys and those prepared using controlled atmosphere melting are compared and the results tabulated to indicate the superiority of controlled atmosphere melted alloys.

(*Authors*)

Report by J. F. Nachman & W. J. Buehler *U.S. Naval Advance Lab. Rep.* 3607

The Procurement of Some Hitherto Rare Metals — 101/III

See Abstract No.: 47/I

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102/III

Arc Melting of Reactive Metals

United States. The use and relative advantages of cold mould and skull furnaces, vacuum and inert atmospheres, consumable and non-consumable electrodes are discussed. Power requirements are considered and a method of estimating pumping speeds is described. The cold mould process is suitable for melting almost any metal or alloy regardless of its melting point or degree of reactivity. It can also be used to provide extremely pure ingots of any cold ductile metal produced as crystal bar by the halide decomposition method. Cold mould arc melting should be suitable for the rare earth metals, and is believed to be replacing or supplementing vacuum induction melting for uranium and thorium. The process has recently been used for re-melting iron, nickel and cobalt base high-temperature alloys containing high percentages of reactive metals such as aluminium and titanium. An advantage of skull furnaces is that the charge to be poured is all molten at one time so that, if stirring is provided, alloy homogeneity is assured. It also permits the pouring of shaped castings. Two advanced types of skull furnace, operated by the Bureau of Mines, are water-cooled, copper, consumable electrode furnaces, one bottom-pour and one tilt-pour. These are operated at a pressure of about 30 mm. Hg. In general vacuum melting is preferable to argon melting since it permits hydrogen removal and, in some cases, deoxidation by carbon. Provided the power supply is adequate the vapour of the metal being melted is always sufficient to support even a d.c. arc. Adequate power can be obtained with consumable electrodes of almost any metal, but may be difficult to achieve with permanent electrodes. In some cases the presence of argon is necessary to prevent vaporisation of volatile alloying constituents. Preliminary furnace evacuation is recommended, however, even though inert gas is used during melting. Most permanent electrode furnaces work best in the pressure range 200–760 mm. Hg, but one type can be operated in vacuum. This incorporates a cooled, large diameter, cathodic, permanent electrode and a magnetic stirring coil to collimate the arc. Sufficient power is obtained at the bath to maintain a shallow pool in vacuum, but the division of power between electrode and bath is inefficient. Good power division is important in permanent electrode melting to get the greatest possible bath volume without excessive electrode erosion. Tungsten electrodes have been found more efficient than graphite. In a 10-lb. permanent electrode skull furnace better efficiency has been obtained at 250 mm. pressure with 20–30 kW than at lower pressures with 35–40 kW. This is probably due to a difference in power rather than pressure but the higher pressure gives less electrode loss per lb. of metal melted. A higher proportion of the power goes into the bath in vacuum than in argon melting. This should result in greater super-heat in skull furnaces and vacuum melting should therefore give good mould filling properties as well as low hydrogen content. Some data on the efficiency of cold mould consumable electrode arc melting are given in tabular form. Defects in consumable electrode melts may be caused by failure to taper off the power at the end of a run, the use of too low a power for a given mould size or the use of too long an arc. Vacuum melting produces smoother ingots than argon melting. Steep thermal gradients exist in both vacuum and argon melting and limit the amount of hardening alloying elements which can be added without causing ingot cracking. Minimum pumping speeds for consumable electrode vacuum melting are calculated on the assumption that only one type of gas is evolved by the metal and no gas by furnace parts.

Paper by J. L. Ham & C. B. Sibley A.M I.E. Conf. *Nat. Res. Corp.* 19.3.56

103/III

Apparatus for Melting Highly Reactive Metals

United States. An apparatus is described which enables refractory metals, such as titanium, zirconium, or their alloys, to be melted and cast under contamination-free conditions. The undesirable property of molten titanium in attacking and reacting with furnace refractories has been largely overcome by the development of the skull furnace. By this means, titanium is melted, by arc or radiation heating, in a pool which is separated from the crucible walls by a skull of unmelted titanium. The problem of the harmful absorption of gases has been overcome by working in an atmosphere of inert gas, *e.g.* argon. With the radiation-type skull furnace, the problem remains that the electrically heated resistor bars, which are made of graphite and suspended over the centre of the charge, may be attacked by titanium vapour travelling upward from the molten pool. If the titanium coming into contact with three resistors or with the furnace roof or walls, is allowed to return to the melt, contamination of the charge will result. The present invention makes use of a vapour interception roof placed between the resistors and the melt. This roof protects the resistors and furnace roof from titanium vapour, with the aid of a continuous sweep of argon gas in a partially downward direction. Where the vapour interception roof is made of graphite, a number of methods are employed: for instance the roof is sloped so that condensed titanium drains into gutters and is not returned to the melt. The roof being between resistors and melt, acts also as a secondary radiation heater. The resistors themselves may take the place of the roof by designing them to slope down to the gutters. They may also be placed at the sides of the furnace, above the gutters and directed at the centre of the charge. An alternative arrangement is to have a vapour interception roof composed of a non-contaminating material, *e.g.* molybdenum. The titanium condensate may then be returned to the melt without the possibility of contamination. In all embodiments a suitable sweep of argon gas is said to suppress the upward flow of titanium vapour.

P. F. Darby, W. L. Finlay, O. W. Simmons & Rem-Cru Titanium Inc. 2,745,891

104/III

Rhenium

See Abstract No.: 210/I

105/III

The Present Status of Molybdenum Production

See Abstract No.: 208/I

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Contd.

Abstract No. and References

The Production of High-Purity Vanadium Metal

106/III

See Abstract No.: 191/I

Melting of High-Purity Uranium

107/III

See Abstract No.: 189/I

Method of Preparing Metal and Apparatus Therefor

108/III

United States. A method and apparatus are described for purifying metal having an atomic number of at least 90, in particular uranium, by the thermal decomposition of volatile compounds of the metal. Purification is carried out in a reaction chamber constructed to withstand the temperatures required without reacting with the metals and to sustain the low operating pressure, about 10^{-3} mm. Hg, without leakage of outside atmosphere. The chamber consists of an outer impervious, rigid tube which may be of stainless steel, porcelain, or other suitable material. This tube is lined with a refractory which is preferably calcium beryllate but which, in some cases, may be alumina, thoria or other coating. The chamber is heated by an electric furnace or furnaces in such a way that a temperature gradient is set up ranging from a lower temperature or vaporisation zone below the melting point of the metal to a higher temperature or decomposition zone above the melting point. Insulation is packed around the furnace and chamber. Halogen vapour for forming a volatile, thermally decomposable halide of the metal to be purified can be introduced into the low temperature zone of the chamber. A sweeping gas, such as pure hydrogen, can also be introduced with the halogen. The outlet of the high temperature zone is connected to a mercury diffusion pump. The impure metal is placed in the vaporisation zone and the system is evacuated and cleansed by washing with hydrogen. The temperature in the vaporisation zone should be arranged to give a maximum rate of volatile iodide production. This can be determined empirically. The decomposition zone is heated to a temperature high enough to decompose the iodide vapour and cause deposition of pure, massive metal on the walls of the chamber. The sweeping gas carries the gaseous decomposition products through the chamber and also combines with excess halogen to render it inactive with respect to the metal already deposited. Hydrogen may also assist the reaction in the vaporisation zone by forming a metal hydride as an intermediate step in the production of a metal iodide. In the case of uranium the use of hydrogen greatly increases the yield of iodide, but in some cases the use of an inert gas or iodine vapour alone may be sufficient. In a particular example quoted a 50 g. mass of uranium was placed in the chamber and heated to 1,000–1,100°C. Hydrogen at the rate of 5 c.c./min. and iodine vapour from a source of iodine at 30°C were introduced together into the chamber and passed over the uranium, the pressure being maintained at about 10^{-3} mm. Hg. This operation was maintained for a period of 5 hrs. during which 25 g. of the impure uranium metal were volatilised and 8.29 g. of spectrographically pure uranium metal were deposited in the form of a mass, and not as a powder, on the wall of the chamber, about 2 inch. from the impure metal. It is believed that the remainder of the volatilised uranium was volatilised at UI_4 but immediately decomposed to UI_3, a non-volatile uranium iodide. The UI_3 can, however, be recovered and converted into UI_4.

G. Derge & G. P. Monet & U.S. Atomic Energy Comm *U.S. Pat.* 2,743,173

Melting and Fabricating Binary Uranium Alloys

109/III

See Abstract No.: 190/I

An Investigation of the Iodide Method of Refining Zirconium

110/III

Russia. In the experiments crude zirconium and a sealed phial of resublimated iodine, or in some cases iodide, were placed in a glass or quartz vessel about 520 mm. long and 80 mm. dia. at its widest section. The apparatus was evacuated to 10^{-4} mm. Hg at a temperature which exceeded by 50° or 60° the maximum vessel temperature to be used during the experiment and was then sealed. The iodine was released by breaking the phial and the apparatus was heated in an oven. Refined zirconium was deposited on a tungsten filament, 0.1 mm. in dia., connected to molybdenum wires sealed into the apparatus. By using three molybdenum wires and two filaments, two experiments could be carried out without recharging the apparatus. Tests were made to determine how the rate at which zirconium was deposited on the filament was influenced by the temperature of the filament, the quantity of iodine, the vapour pressure of tetraiodide and the temperature of the vessel, *i.e.* the temperature of the crude zirconium. The rate of deposition was found to be markedly dependent on the vapour pressure of ZrI_4 and was a maximum at a tetraiodide vapour pressure of about 2.5×10^{-1} mm. Hg. If the results obtained hold for larger industrial equipment it would be possible to control the refining process by using a reaction vessel equipped with the means of obtaining and controlling the required pressure. When the apparatus was kept at a constant temperature (260°C) the rate of deposition was found to increase with increase of filament temperature up to about 1,450°C. The rate then ceased to increase possibly because the vapour pressure of iodine is then many times higher than that of ZrI_4. The rate was very sensitive to temperature variations at about 1,300°C when the vapour pressures of ZrI_4 and iodine were very close, at about 0.35 mm. Hg and 0.4 mm. Hg respectively. The rate of deposition was greatest when small quantities of iodine were used and this effect is also attributed to the influence of vapour pressure. Experiments to determine the effect of the vapour pressure of tetraiodide on the rate of deposition were made in a vessel equipped with an auxiliary arm which protruded out of the oven during the heating process. The vessel temperature was kept constant at 300°C and the vapour pressure of tetraiodide in the reaction chamber was altered by varying the temperature of the auxiliary arm. Investigations of the effect of vessel temperature on the reaction rate showed that the rate increased with vessel temperature up to about 230°–250° and then decreased rapidly due to an increase of tetraiodide vapour pressure.

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Further heating caused deposition to recommence and the rate rose to a second maximum. A separate study of the high temperature maximum was carried out using a silica reaction vessel. This was connected to a short U-shaped tin manometer through a filter consisting of a piece of tube filled with zirconium filings. The manometer acted as a null instrument, the pressure inside the reaction vessel being balanced against a pressure of argon measured by an ordinary mercury manometer. The second maximum is attributed to the existence of a lower iodide which has a dissociation vapour pressure in the temperature range 500°–600°C equal to the optimum pressure. When the tetraiodide vapour pressure was kept at a constant optimum value, no decrease in rate of deposition was observed up to a vessel temperature of about 700°C.

Article by V. S. Emelyanov, P. D. Bystrov & A. I. Evstyukhin *J. Nuclear Energy* 3, August 1956 121-131

111/III **The Dissociation Pressures in the Zirconium—Oxygen System at 1,000°C**

See Abstract No.: 194/I

112/III **The Melting and Casting of Titanium**

See Abstract No.: 197/I

113/III **Titanium and Vacuum Heat-Treating Furnaces**

United States. Various known types of vacuum annealing furnaces suitable for the treatment of titanium are described. One type is the standard bell furnace normally employed for laboratory work only. Another is the pit-type furnace and a third is the so-called three stage semi-continuous vacuum furnace, where the work, by means of gate valves, is placed into, and withdrawn from the heating chamber without breaking the vacuum in the latter. These three so-called hot-retort furnaces have inherent disadvantages as the service life of the retort is limited. This difficulty is largely overcome in the Kold-Retort furnace where the heating elements are inside the retort and radiation fields are employed for thermal insulation thus eliminating the necessity for refractory brick linings. A major problem encountered in the design of this furnace is the choice of the alloys which should be a material of low vapour pressure. At present these furnaces are fitted with molybdenum or Hipernik. As heating elements frames from Hipernik are expensive, research is in progress to find cheaper new alloys with the same properties. The charge space of the furnace is as large as $4 \times 4 \times 15$ feet. A temperature of up to 3,000°F can be obtained.

Article by R. R. Giler *Westinghouse Engr.* 15, Nov. 1955 194-201

114/III **Vacuum Fusion Analysis of Titanium, Zirconium, and Molybdenum, Determination of Oxygen by the Iron Bath Technique**

United States. To determine the oxygen content of metals, two vacuum fusion techniques are available, the iron bath and the Walter or dry method. The former, in which molten iron in a graphite crucible is the reduction medium, is suitable for most metals, but has been shown by some workers to give low oxygen values for titanium and zirconium. This led to the development of the alternative method. As the authors required an analytical technique of general application, the reasons for these low values was investigated and found to be that the molten iron, used to dissolve the material and allow the oxides in it to reach the graphite and be reduced, absorbed carbon from the crucible and solidified. Solidification was reported by Smith (*Analyt. Chem.* **27, 1636**) to start at the surface, but induction heaters working at 500 kc and 30 kc were found not to disturb the surface of the iron bath and prolong its life, though the latter frequency could agitate the surface of a tin bath. Workers who achieved success in these analyses were found to have used larger crucibles, liberal additions of iron and tin between samples or to have wrapped the sample in iron foil. All these practices would result in keeping the bath longer molten. As no known crucible material is insoluble in the bath, the authors have devised an analytical procedure in which all measurements are taken before the bath solidified. They used an air-cooled furnace similar to that described by Guldner and Beach (*Analyt. Chem.* **22,** 366). Gas evolved in the furnace is pumped by a mercury diffusion pump into the analytical system where it is collected and measured by oxydising the carbon monoxide produced in the furnace to carbon dioxide at 300°C. The gas so formed is collected in a liquid nitrogen cooled trap and all non-condensable gases are rejected. The liquid nitrogen is then replaced by a methanol slush and the gas volatile at the melting point of methanol is considered to be carbon dioxide. To prepare the bath for a determination the furnace was pumped to below 1 mm. Hg and the temperature of the empty graphite crucible raised to 2,300°C to outgas it. When the blank rate had fallen below 5 litre-microns/hour at 1,800°C the temperature was lowered to 1,400°C and 10 grams of iron added for the bath. When outgassing at 1,800°C is complete, the temperature is lowered to 1,200°C and 10 grams of tin are added. The temperature is then returned to 1,800°C and in a few minutes the bath is ready for the specimen. The blank rate is checked before each sample run by noting the pressure rise in a fixed volume into which the gases from the furnace are pumped. This procedure takes only two minutes. The furnace temperature is then lowered to 1,600°C and a sample (0.25 g. of titanium or zirconium, or 1 g. of molybdenum) together with 1 to 3 g. of NBS steel No. 4 are added. The test is carried out at a temperature of 1,800 °C. This is above the minimum for the reduction of the oxides and is sufficiently low to prevent rapid solidification of the bath. 30 minutes later when gas evolution is complete, a further sample of NBS steel No. 4 is analysed. Gas evolution in excess of that expected for this steel shows imperfect reduction of the original metal sample and the excess gas production is added to the volume for that sample. Further additions of NBS steel No. 4 are then made till this evolution is finished. A smaller gas production when the NBS steel sample is added, indicated gettering of the gas by active films of metal. This effect has been investigated and it is shown that tin improves the recovery by covering these active surfaces. Up to four samples can be analysed in each bath before solidification, additions of tin and steel being made between each sample.

Article by R. S. McDonald, J. E. Fagel & E. W. Balis *Analyt. Chem.* 27, Oct. 1955 1632-1636

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Titanium Alloy Reclamation by Vacuum Annealing

115/III

United States. It was only fairly recently that the cause of the erratic ductility, delayed cracking and thermal instability in titanium alloy components was traced to excessive hydrogen content. In the meantime large quantities of hydrogen-embrittled components had been scrapped and had to be re-claimed. This was achieved by vacuum annealing to reduce the hydrogen content to the safe level which is now maintained in the production of all titanium alloy parts. Tests showed that although ductility could be restored by annealing in either air or vacuum, the material treated in air embrittled rapidly at temperatures above 600°F. whilst the heat treatment in vacuum eliminated most of the instability. Micro-structure examination and tensile and notch-rupture tests showed that vacuum annealing can be expected to improve not only the low-temperature ductility properties of the alloy, but also its thermal stability—a desirable effect in many elevated temperature applications. The cost of vacuum heat treatment of titanium parts depends on the length of the cycle and the temperature required, which in turn are determined by the sizes of the parts and whether they must be stress-relieved or degassed. An average figure for stress-relieving compressor blades between 3 and 12 inch. long is 0.22 to 1.35 dollars per blade; embrittled blades of the same size can be degassed and annealed for from $0.45 to $3.30. One organisation in the U.S.A. has re-claimed, mostly for jet aircraft manufacturers, nearly one million £ worth of hydrogen embrittled titanium scrap by means of vacuum heat treatment and records show almost 100% success. Degassing cycles vary from 3 to 36 hours at temperatures ranging from 1,250 to 1,800°F, depending on the contamination, *e.g.* jet engine discs weighing 72 lbs. were degassed by holding at a temperature of 1,250°F under a vacuum of less than 1 μ for 36 hours. Pressure increased to about 600 μ during the first few hours due to rapid evolution of gas and then slowly decreased. After 36 hours the discs were cooled to below 500°F in 3¼ hours, the diffusion pump was shut off and the retort cooled with a fine water spray. The vacuum-tight retort is subjected to high temperatures and must resist scaling and frequent thermal shock. Retorts made of Inconel are still in good condition after 5,000 hours of service.

Article by D. N. Williams, R. I. Jaffee & C. A. Bentley, Jr. *Metal Progr.* June 1956 57-59

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Hydrogen Embrittlement of a Commercial Alpha-Beta Titanium Alloy

116/III

United States. It is known that hydrogen embrittles α-titanium by elevating its transition temperature, probably as the result of the formation of titanium hydrides. Thus, hydrogen acts like nitrogen, which is also an interstitial contaminant. On the other hand, β-titanium will tolerate large amounts of hydrogen without suffering mechanical damage. In the important commercial α–β alloys, formed by mixing these two phases, hydrogen produces embrittlement, although the mechanism is not of the same type which produces embrittlement in α-alloys since ductility damage increases as the strain rate is reduced in α-β alloys, whereas the embrittlement in α-alloys increases as the strain rate is increased. The behaviour of the α-β alloys is similar in this respect to that of steel. The article describes experiments carried out on α-β titanium 140 A with three different hydrogen contents. The tensile properties of two *as-received* rods and one vacuum annealed rod were measured over a range of testing temperatures and strain rates. The hydrogen content of the two *as-received* rods were 270 and 310 p.p.m. respectively, the vacuum annealed rods had hydrogen contents between 92 and 170 p.p.m. Graphs are given showing the experimental results. It is stated that the results confirm that the embrittlement seems to result from the same mechanism which produces hydrogen embrittlement in steels and that it is consistent with a competitive rate theory such as suggested by Zapffe, or by Petch and Stables.

Article by R. J. Ripling *J. Metals* May 1956 502-503

Determination of Hydrogen in Titanium Metal by Hot Extraction

117/III

United States. A method and apparatus for the determination of hydrogen in titanium metal are described. Samples of sponge, ingot drillings, sheet, or solid stock are vacuum hot-extracted at 900° to 950°C, and the pressure and temperature of the collected gas, known to be pure hydrogen, are measured in a known volume. The hot extraction of sponge, ingot drillings, or thin sheet is generally complete in 15 minutes. Thick solid samples require a longer time to complete the hot-extraction process.

(*Authors*)

Article by R. K. Young & D. W. Cleaves *Analyt. Chem.* 28, March 1956 372-374

The Routine Determination of the Hydrogen Content of Aluminium and Aluminium Alloys by the Hot-Extraction Method

118/III

United Kingdom. In the apparatus described gases are extracted from a solid specimen of aluminium or aluminium alloy by heating it in a vacuum at a temperature below the solidus. The extracted gas is pumped to an analytical system where it is stored at low pressure (generally less than 50 μ) until extraction is complete and analysis can be carried out. A vacuum drill is also described which makes it possible to penetrate pores or blisters in defective metal and release the gases contained in them to the analytical system of the apparatus. The total volume of gas evolved in a test run is very small, *e.g.* 0.01–0.05 c.c. at S.T.P. from a cylindrical sample 10 mm. in dia. by 40 mm. long. It is therefore necessary to avoid spurious evolution of gas. The method has the advantage that the evaporation of volatile elements from the specimen is low at the temperature used. The extraction tube is made of silica and its shape is such that if evaporation does occur condensation is limited to a portion of the tube that can be pre-baked before use. Reaction between condensed elements and water vapour adsorbed on the surface of the tube is thus avoided. Care is taken to clean the specimen, which may be solid, strip or wire metal, immediately before use. Tap greases which give off organic vapours are avoided. The sample is placed in the extraction tube which plugs into a standard B.24 interchangeable water-cooled joint approx. 1 inch in dia. This joint leads, *via* a tap and a liquid air trap, to a 2-stage mercury diffusion pump which pumps the gas evolved from the specimen into a calibrated container. A McLeod gauge with a maximum pressure range of about 70 μ is used for measuring the pressure. The analytical system contains a platinum filament, a

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palladium tube and a Pirani gauge which is used for observation purposes. A small side tube is used to freeze out condensable gases. The whole apparatus can be evacuated by a 3-stage mercury diffusion pump backed by a standard laboratory vacuum line maintained at 1–2 mm. Hg. The extraction system can be evacuated without admitting air to the analytical system. With the specimen held close to the B.24 joint the apparatus is evacuated and the extraction tube is baked by flaming out or by heating with a radiation oven. During this time the palladium tube and the platinum filament are conditioned. A cut-off test is made and the sample is then moved to the end of the tube and the extraction furnace is slid into position. An external extraction furnace has so far been found the most suitable, despite the time taken to attain temperature, but experiments with high frequency heating show promising results. Liquid air is placed in the traps and extraction is continued until the pressure in the analytical system is constant. Analysis is then carried out. Finally, air is admitted to the extraction system by breaking a glass 'pip' which is immediately re-sealed. Reproducible results have been obtained with this apparatus which agree well with independent measurements made by other methods. The vacuum drill constructed for use with the apparatus consists of a $\frac{1}{16}$-inch twist drill operated by hand by means of a knob on the end of a bent, stainless-steel spindle. This spindle is hollow to facilitate pumping. From the knob it passes through a non-rotating flexible bellows, a copper Pyrex seal, a Pyrex glass tube and a B.24 conical joint into the specimen compartment. Specimens are brought into this compartment through a wide conical greased seal. The whole apparatus connects into the analytical system described above. A metal bellows is used to give this connection some flexibility. The specimen is held on an anvil which can be manoeuvred magnetically to bring the defective area under the drill. Three units of the type described have been in operation for two years without any need for modification.

Paper by C. E. Ransley & J. D. Talbot *J. Inst. Metals* 84, July 1956 445-452

119/III

Effect of Vacuum Degassing on Properties of Various Aluminium Alloys

United States. Gas porosity can be eliminated from non-ferrous castings by holding the melt in a vacuum chamber for a period of 5–10 mins. prior to pouring. The improvement which this degassing process effects on the mechanical properties of aluminium alloy castings has been investigated. The additional effects of section thickness, mould material and the use of refining agents have also been studied. Five different aluminium alloys were tested. Step castings ranging from $\frac{1}{4}$–2 inch. thick were made in both sand moulds and grey iron chill moulds. Separately cast test bars were also made. Seventy pound heats of each alloy were melted in a high-frequency induction furnace. A set of castings was poured at 1,250°F with non-vacuum-treated metal. The remainder of the melt was returned to the furnace, superheated and held in the vacuum chamber for 12 minutes at a pressure of about 0.3 mm. Hg. A second set of castings was then poured at 1,250°F. This degassing procedure does not require the expensive equipment generally associated with vacuum melting. A mechanical pump is sufficient to reduce the pressure in the chamber to the 0.2–0.4 mm. Hg range required and the time taken is less than is often required for conventional inert gas flushing for removing hydrogen. Half the original melt was treated with titanium grain refiner and sets of vacuum treated and non-vacuum treated castings were also poured with this metal. Specimens were machined from all the castings and were treated for tensile strength, yield strength and elongation. Vacuum degassing resulted in improved properties in each type of casting except in those poured from an alloy of composition Mg-0.60%, Zn-5.3–5.4%, Cr-0.50%, Ti-0.20%. In this case the elongation values were slightly lowered although yield and tensile strengths were markedly improved. Vacuum degassing alone does not result in the optimum possible properties. Grain refining additions are necessary in sand-mould castings but are less important for chill-cast alloys. Because of their high thermal conductivity aluminium alloys tend to solidify uniformly throughout the casting section. This makes it difficult to feed additional metal into the casting as it contracts and microshrinkage voids may develop. The effect is more noticeable in thick sections. It can be off-set by using moulds of high thermal diffusivity, *i.e.* chill moulds, and by using alloys having short liquidus to solidus temperature ranges. The advantage of these practices, however, cannot be fully utilised unless the melt has been adequately degassed.

E. E. Layne & H. F. Bishop *U.S. Naval Research Lab. Rep.* No. 4797 10.7.56

120/III

Study of the Degassing of Metals

France. The technical and economic success of mass production of vacuum tubes and gas filled discharge tubes depends upon the safe, thorough degassing at maximum speed and above all on the degassing of the metal constructional parts of the thermionic tube. In the present paper a systematic description is given of the most important methods of degassing of metals which have proved useful in modern valve production. Details are given of vacuum furnaces suitable for the purpose. Finally, the technique of degassing with a tube connected to the pump is discussed in detail and examples taken from shop practice are quoted.

Article by O. Winkler *Rev. Metall.* 52, Dec. 1955 934-942

121/III

Methods and Techniques for the Degassing of Metals I.

Czechoslovakia. The technical and economic success of mass-production of vacuum-tubes depends upon thorough and speedy degassing of the valve system. Whilst the gases and vapours adsorbed on glass surfaces are fairly readily removed by baking, the metallic material in the system may hold relatively large quantities of occluded and chemically bound gases, which will be given off quite slowly. The gases contained in metals are most commonly H_2, N_2, O_2, CO, CO_2. These gases are mainly taken up in the smelting process, but may also be absorbed in the solid state. As a first measure against undesirable gas evolution of metals used in the tubes the metal should have been degassed by melting in high-vacuum prior to use. Although vacuum-molten metals are costly and supply is limited at present, the prospects for the increasing use of such materials are now very great. Vacuum-melted and cast metals are softer than conventional metals due to avoidance of oxide formation. Since vacuum-molten metals are at present costly, and contamination may still occur during manufacture of

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valve-parts, the single parts of the system undergo a pre-degassing process before assembly. This process consists of heating the parts in an oven under high vacuum or in an atmosphere of H_2. H_2 degassing is cheaper, quicker and protects parts from air-penetration during storage. It is widely used for mass production of radio valves. However, vacuum-degassing is essential in many cases, when the presence of hydrogen or of water or oxygen contaminants is undesirable. In some cases no pre-degassing is desirable, *e.g.* in the case of wire-cathodes and cold stressed parts of the valve. High vacuum degassing is carried out at ca. 10^{-3} mm. Hg and up to 1,100°C. The furnaces are such that the whole process can be carried out within 24 hours. Rotary oil pumps are usually sufficient for the evacuation. For complete degassing, or for graphite and tantalum, higher temperatures of 1,800–2,400°C are required. The disadvantage of most furnaces is the time of the degassing process. This is usually a minimum of 20 hours, of which 15 hours may be cooling-down time. A quick process used in English valve factories, reduces this time by using transportable quartz tubes which are inserted into the oven for up to 2 hours, then removed and cooled in an hour. Radiation-cooled high-frequency furnaces achieve shorter degassing times for small quantities of metal. Pre-degassing by heating in a hydrogen current is the more convenient process and is more suitable for continuous manufacture. Hydrogen furnaces working at over 1,800°C are in use. The purity of the hydrogen is of great importance. Hydrogen degassing is not to be used with metals which deteriorate markedly, *e.g.* Ta, Cu, Ti, Zr, etc. All pre-degassed parts, whether hydrogen or vacuum-treated, require careful handling, storage and assembly. Handling with tweezers or sulphur-free rubber gloves is essential. Storage can be in bags, nitrogen-filled jars, evacuated desiccators sealed tubes or best of all, evacuated bottling jars.

Article by W. Espe *Vakuum-Tech.* 3, May 1956 39-53

Methods and Technique of Degassing Metals II. 122/III

Czechoslovakia. An important method of overcoming the deleterious effect of gases contained in metals used in vacuum tubes is that of degassing during the pumping process. This is necessitated by the high operating temperatures of some electrode parts, by contamination during assembly, and by the cost of high-temperature pre-degassing furnaces. The temperature at which the electrode system may be degassed is limited by metal vapour deposition and by mechanical stability. Temperature control is therefore critical and is mostly achieved pyrometrically. Four different methods of degassing during the pumping process are available, namely (*a*) furnace heating, (*b*) resistance heating, (*c*) high frequency heating and (*d*) electron bombardment. These may be combined in various ways. The energy supply necessary in the last three methods will depend upon the electrode constants. External heating during pumping is carried out by electric or gas-heated box furnaces, or in an automatic process, by heating tunnels. The metal parts are less effectively degassed than the glass surfaces. Noticeable degassing of metal parts not pre-degassed, in contact with glass surfaces, takes place, however. Externally accessible metal parts may be heated by separate heating coils. Reduction of oxidised surfaces, *e.g.* Cu, in contact with glass, may be achieved by pumping out at 550°C. The use of hard glass and an evacuated furnace avoids collapse of the tubes. Degassing of filaments, cathodes etc. may be carried out before degassing of other parts by direct passage of current. Degassing by high-frequency heating makes use of the heating of the electrodes by the field of an external coil or winding. Frequencies up to 8×10^5 c/s are used. The source of field energy is chosen having regard to the nature of the electrode, *e.g.* dimensions, specific resistance and emissivity. Rise in gas pressure may be quite rapid with h.f. heating. Short degassing times may be achieved by 'shock' heating, which also safeguards glass walls from softening. In some cases the high temperature 'shock' heating of specific parts is undesirable, since the released gas may react or be absorbed by cooler parts, as *e.g.* tantalum. An indication of excessive gas congestion is given by the intensity of the glow discharge, which must never be allowed to change into an arc discharge. Maximum h.f. degassing temperatures are around 850°C. High frequency heating of electrode systems with metal envelopes is not possible. In vacuum tubes with a sufficiently strong electron-emitting source, degassing by electron bombardment is feasible. A potential is applied to the electrode which is positive with respect to the electron source. The electron current energy heats and degasses the electrode. The method is very efficient since it approaches the conditions of the operating state. Inaccessible electrode parts can be heated in this way. Bombardment degassing is also used for pre-degassing systems with large masses of high m.p. metals (*e.g.* W, Ta, Mo). This is carried out in evacuated metal envelopes and thus temperatures up to 2,500°C may be employed. Moreover, faults may be recognised before the final fusing into the glass envelope. Electron bombardment in thermionic tubes must be carried out below a certain pressure, otherwise damage by ion bombardment or arc formation may result. Current-limiting resistances in the form of tungsten filament lamp combinations are therefore included in the discharge circuit. Bombardment degassing is indispensable for larger thermionic tubes, and where oxide cathodes are employed the method serves to activate the cathode layer. It is no longer usual to degas the electrodes of smaller oxide-cathode tubes, by electron bombardment, and any gas liberated after sealing off must be absorbed by the getter.

Article by W. Espe *Vakuum-Tech.* June 1956 69-82

Vacuum Distillation of Metals I. Theory 123/III

United Kingdom. The distillation of metal proceeds at a rate dependent on its vapour pressure, the pressure of the residual gas and the concentration gradient of the evaporated metal atoms between the surface of the evaporating liquid and the condenser. Due to the low temperature of the condenser re-evaporation is limited and this results in a pressure gradient in that space which determines the net distillation rate. Where the residual gas pressure is so low that only relatively few collisions occur between the vapour atoms and the gas molecules the conditions are known as molecular distillation. However, normally distillations of metal are carried out in a pressure range somewhat above that of the molecular range. The advantages of vacuum *versus* atmospheric evaporation are: (*a*) the net evaporation rate is increased; (*b*) a better separation of volatile components is achieved; (*c*) contamination by oxidation is reduced and (*d*) reduction processes involving a volatile phase can be operated at lower temperatures. The author proceeds to discuss vapour pressure and associated with it the

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Clausius-Clapeyron equation, Raoult's law and Henry's law. If in a binary mixture one component present in small amounts exerts a higher pressure than would be predicted by Raoult's law then the pressure of the other component will also be higher. This may result in the formation of a azeotropic mixture, *i.e.* a mixture having a minimum boiling point. Such mixtures can never be separated completely but as the composition of an azeotrope generally alters with variation in pressure an alteration of the pressure-temperature conditions may make separation possible. Under molecular distillation conditions azeotropes cannot occur. It follows a discussion of the term 'Relative volatility'. In a table reproduced below the vapour pressure ratios existing

Vapour Pressure Ratios

Volatility Ratio, Metal X/Aluminium at 800°C (Assuming Raoult's Law)			
Hg:	8.5	×	10^{10}
Na:	4.0	×	10^{8}
Mg:	3.0	×	10^{7}
Zn:	2.2	×	10^{7}
Li:	2.8	×	10^{6}
Ca:	1.8	×	10^{5}
Mn:	73.50	×	
Al	1.00		
Cu:	0.15		
Si:	0.11		
Fe:	1.3	×	10^{-3}

Article by A. J. Martin *Metal Industr.* 88, 8.6.1956 473-477

between various metals at 800°C are shown, taking the v.p. of aluminium as unity. Normally the condenser temperature is below that of the melting point of the distillate. But there are cases where partial condensation is applied in order to assist separation of two or more components. This is effected by keeping the condenser temperature at the evaporation temperature of the more volatile component thus promoting re-evaporation of the same, while the other is being deposited on the condenser.

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Vacuum Distillation of Metals II. Practical

United Kingdom. Vacuum distillation may be divided into three processes: (*a*) Reductions, (*b*) Purifications, (*c*) Miscellaneous Applications. These are considered in turn. (*a*) High costs have limited commercial application of vacuum in many processes but vacuum assisted evaporation of zinc in a continuous process has been used for many years and reduction of magnesium by silicon under vacuum by the Pidgeon process enables the reduction temperature to be lowered from 2,300°C to 1,100°C and direct reduction of dolomitic ore can be carried out. The article illustrates the type of retort in use for this operation. 75% of the magnesium can then be collected provided that the collecting temperature is sufficiently high. A similar method can be used for producing lithium from spodumene ore, a large excess of lime being added during the process. 90% of the total lithium content is then collected at a temperature of 450°C. Barium has been produced by the Matignon technique. Fine barium oxide and aluminium powders are compressed into pellets. Reduction occurs at 600°C and 0.5 mm. Hg pressure. Calcium can be produced from its oxide by vacuum reduction with aluminium. (*b*) Vacuum distillation is used more frequently for purification purposes than for metal production. The process is only worthwhile where at least one of the following advantages accrue: (1) Complete separation of two components without further processing, (2) Separation of impurities from a highly electronegative material which would otherwise require expensive refining techniques. (3) Prevention of oxidation. (4) Prevention of metal losses. (1) applies to the process, developed by Broken Hill Associated Smelters, of recovering 90% of the Zn from Pb. (2) was the main reason during the last war, for purification of aluminium scrap by distillation. The mercury process and the Beck process were used and are described in detail, (3) Is the reason for the refinement of titanium, zirconium, hafnium and tantalum by the Kroll process, and (4) applies to the recovery of silver from zinc, lead, silver crusts effected in the Parkes process.

Article by A. J. Martin *Metal Industr.* 15.6.1956 495-498

125/III

High Vacuum Distillation Apparatus

See Abstract No.: **134/III**

126/III

The Evaporation of Impurities from Silicon

See Abstract No.: **136/I**

127/III

Investment Casting of Vacuum Alloys

United States. Developments towards investment casting of vacuum-melted alloys on a commercial scale are described. Investment casting is the only major casting method which can be used without basic revisions for vacuum-casting iron, and nickel and cobalt alloys. The alloy may be prepared and cast in one vacuum unit or a previously prepared alloy may be re-melted and poured either in an inert gas or under vacuum. The inert-gas method can sometimes be used with existing equipment and can give high production rates. With high-tem-

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perature alloys containing aluminium and titanium the properties may compare favourably with those achieved by vacuum-melting. It is difficult, however, to control the effectiveness of the blanket of inert gas and, unless the furnace is air-tight, gas losses cause high melting costs. With some alloys such as high temperature alloys which do not contain aluminium and titanium, the high properties of the vacuum-melted alloy are almost lost on re-melting in argon. A vacuum furnace for alloy production and investment casting has been developed by the Cannon-Muskegon Corp. This consists of a tank 6 ft. in dia. and 7 ft. long which contains an induction furnace of 400 lb. capacity. Power is supplied by a 100-kW, 3,000-cycle motor generator set and the system can be evacuated to less than 10 μ for pouring. A 3-ft. dia. mould table in front of the furnace can be rotated through a vacuum seal. Moulds are placed on the table and are rotated in turn under the furnace for pouring. A seal allows for rotation for centrifugal castings at speeds up to 800 r.p.m. Provision is made inside the tank for pre-heating and cooling the moulds under vacuum. It has been found that heating times in the vacuum furnace can be reduced and gas contents more easily controlled by first preparing a suitable base alloy in air. After re-melting in the vacuum furnace this metal is deoxidised with carbon and alloying additions of boron, aluminium and titanium are made as required. Trouble due to the outgassing of the mould during pouring is reduced by pre-heating the mould in vacuum. This trouble may also be lessened by placing a pouring cup on the mould and raising the riser a few inches, or by providing suitably placed vents. A 50-lb. vacuum melting furnace for investment casting has been produced by the Consolidated Vacuum Corp. The charge of 50-lb. can be melted in 30–40 mins. with a 30-kW generator and the chamber pressure can be reduced to less than 10μ in 3–4 mins. Alloying elements can be added inside the furnace and provision is made for temperature measurement, sampling, and heating and cooling moulds. The vacuum chamber holds 2–3 investment moulds and 6–9 moulds can be produced per hour. A new 8-lb. vacuum furnace has been designed by F. J. Stokes Co. for re-melting and casting vacuum-melted alloys. The charging chamber and the furnace are loaded with separate slugs of vacuum-melted material. A hot investment mould is placed in the chamber which is then evacuated to less than 10μ. The furnace charge is melted in about 3 mins. and poured. A cold slug is then moved into the furnace from the charging chamber to cool the furnace to a non-oxidising temperature. After a wait of about 1–2 mins. the chamber is opened and the mould is removed. This furnace can pour 10 × 10 × 10 inch. moulds at a rate of 8–10 per hr. and may possibly be used with existing generating equipment. For certain applications investment-cast vacuum alloys should do as well or better than wrought vacuum alloys. Future developments may bring the cost of the castings to less than twice the cost of comparable air-melted castings.

Article by F. K. Iverson *Foundry* August, 1956 119-120, 122, 124, 126 & Article by F. K. Iverson *Iron Age* 178, 19.7.1956 120-122

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Recent Developments in the Art of Precision Casting

128/III

United States. In conventional investment casting disposable patterns of wax, plastic or, in some cases, frozen mercury are generally used. Developments in this field include a greater use of steel dies, wax injection at higher pressure and modifications in precoating and investing to produce stronger moulds. As a result the production of castings weighing 1–10 lb. or more is increasing, although most precision castings are still in the 1–4 oz. range. Advantages of precision casting are its ability to cast alloy compositions which are difficult to machine or forge, and to prove a cast structure with better high-temperature creep-resistance and rupture strength than comparable forged compositions. Recent developments in vacuum melting, vacuum melting and casting, and casting of vacuum-melted alloys in an inert-gas atmosphere have increased these advantages, and the use of vacuum techniques has become standard practice in many precision casting foundries. Improved properties and soundness, especially freedom from gas pinholes at the surface, have been obtained by vacuum-casting aluminium alloys, brasses and bronzes which have been air-melted. Precision casting also shows promise for titanium in small section thicknesses. New methods of precision casting include the Investment-X Process. In this a disposable pattern is used but the usual investing process is avoided by coating the pattern with a fine silica composition bonded with tetra-ethyl silicate. This is stuccoed with a coarser refractory for mechanical strength, and tunnel-dried. From five to eight refractory layers are applied according to the size of the casting, and the wax is finally dissolved out at room temperature. Large castings can be made in this way and the rapid radiation of heat from the thin shells should result in fine grain and low decarburisation. Trouble may be caused by the high coefficient of expansion of the silica. Two other new methods are the Shaw process and the Glascast process, both of which use a permanent match-plate pattern of wood, plastic or metal. In the former the use of silicic acid gel in contact with the pattern makes it possible to strip mould-sections from the pattern. In the Glascast process plaster moulds are cast which are then used to slip-cast shells. The slip is a water suspension of 'Glascast' powder, a glass with a low expansion. The resulting shells are fired and assembled to form moulds which can be cast hot or cold. Cobalt alloys can be cast in the pre-heated moulds when the metal is up to 3,200°F, without reacting with the mould. The shells may be suitable for vacuum casting because of their small amount of refractory and hence low gas content.

Article by N. J. Grant *Metal Progr.* Sept. 1956 113-117

Impregnation in Modern Powder Metallurgy

129/III

United Kingdom. Some of the materials which can be made by impregnating a metal compact with a lubricant, another metal or a plastic are reviewed. Originally impregnation was used to provide lubricating properties, and a mineral lubricating oil was almost invariably used to infiltrate the porous metal, either by capillary attraction or under a vacuum. One of the earliest products, patented by Gwynn in 1870, was a hot-pressed tin compact containing residues from a petroleum still. The next development was to use an anti-friction metal in place of oil to give a harder and more resistant lubricating surface. A range of infiltrants can now be used to provide either lubricating or other properties. Tungsten oxide impregnated with copper or silver has been used for electrical contacts. Infiltrants used for iron include lead, a copper-iron-manganese alloy and copper. Iron impregnated with copper is found to have better mechanical properties than sintered iron-copper compacts which tend to be brittle. An infiltrated tungsten-nickel compact with a density of 18.1 g./c.c. and a Brinell

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hardness of 330 kg./mm.^{2} has been obtained by placing a compact of 52% tungsten and 48% nickel powder on a tungsten skeleton, the amount of the infiltrant being 13% by weight of the skeleton. The assembly was heated in a hydrogen atmosphere at a little above the melting point of the infiltrant. High-tungsten alloys which are comparatively easy to machine can be obtained by impregnating tungsten with copper. Metal with 83% of the full density of tungsten but which can be drilled, milled or turned with comparative ease has been obtained in this way. Once the copper has fulfilled its purpose it can be completely removed by evaporating it in a vacuum of 10^{-5} mm. Hg for 15 minutes at a temperature of 1,550°C. This treatment ensures that the pores of the tungsten compacts remain open, which is of use in tungsten cathodes for discharge tubes. The use of Fluon; or Polytetrafluorethylene, as an infiltrant may introduce a new range of bearing materials. Impregnation with this plastic, which has one of the lowest coefficients of friction known, has been effected by extrusion of Fluon into the pores of the metal and by impregnation of sintered metal with finely divided Fluon. Another new product made by impregnating metal with plastic is the 'dry' bearing material patented by the Glacier Metal Co. Ltd.

Article by Anon. *Engineer* **202**, 28.9.56 436

130/III **An Improved Method for the Production of Single Crystals of Semiconductor Materials**

See Abstract No.: 137/I

131/III **Spirals Developed on Single Crystals of Copper by Heating to High Temperatures on High Vacuum**

See Abstract No.: 135/I

132/III **High-Temperature Vacuum Furnace for Tensile Testing**

See Abstract No.: 153/III

38 — DISTILLATION — 38

133/III **Estimating Steam Film Coefficients Under Vacuum**

United States. In the process industries it is often necessary to estimate the condensing film heat-transfer coefficient for steam condensing at pressures less than atmospheric. Exhaust steam from turbines, and water vapour from vacuum driers and stills, are nearly always condensed below atmospheric pressure. The equations normally used in estimating this coefficient, for vapours condensing on the outside of tubes, require a knowledge of the temperature of the condensate film and the corresponding thermal conductivity, viscosity and density. Based on the simpler equation covering the conditions at atmospheric pressure, the author developed expressions which make it possible to estimate the condensing film heat-transfer coefficient for steam condensing under vacuum, knowing only the temperature of the condensate film and the condensing load. The calculation is thus greatly simplified and in an example given the deviation from the value obtained using the standard equation is less than 1%.

Note by L. Fan *Chem. Engng.* **63**, April 1956 208-210

134/III **High Vacuum Distillation Apparatus**

United States. The invention relates to an improvement in high vacuum distillation apparatus to separate liquids into their components and is particularly intended for the separation of an isotope of an element from a mixture containing other isotopes. The apparatus consists of a number of evacuated vertical columns each comprising a central glass tube heated by an internal resistance element and surrounded by a cylindrical water-cooled condenser separated from the evaporating surface by a distance of the order of the mean free path of the molecules vaporised from the liquid to be distilled. The bottom of the annular space between the evaporator is divided by means of a ring partition into two annular troughs each connected to an outlet tube in order that the distillate and residue may be led off separately. Disposed below each column is a glass reservoir equipped with an internal electromagnet pump. The output from each pump is fed through a heated tube to the column above it. The reservoir is fed with the distillate of the preceding column and the residue of the next column. This arrangement is continued throughout the sequence of columns. The reservoirs are interconnected by overflow conduits which enable excess liquid to be fed back to the next lower reservoir and re-cycled; this enables the flow of liquid through each stage of the system to be balanced. Data is given for the performance of a ten-column system when distilling uranium pentaethylate in which the uranium was the normal isotopic mixture. Samples taken from the product reservoirs at each end (heavy and light) of the system were analysed by means of a mass spectrometer. It was found that the concentration of the light constituent per column was equal to 0.11%.

S. L. Madorsky & U.S. Atomic Energy Comm. *U.S. Pat.* 2,728,717

135/III **A Vacuum Distilling Apparatus**

Czechoslovakia. Due to the stringent high vacuum requirements considerable difficulty is experienced in practice when designing molecular stills of the centrifugal type for large-scale industrial production and normally it is preferred to operate a series of small units instead of one large unit. This is expensive with respect to first cost and operational cost. In order to overcome these difficulties it is proposed to build large-size units where the centrifugal component and condenser is arranged the conventional way both being housed in an evacuated chamber but providing for the latter to be divided into an upper and lower compartment. The two compart-

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ments are separated from each other by a liquid seal formed by a trough filled with silicone oil, into which dips a flange which forms part of the rotating element of the still. In this manner the actual distillation process can be carried out at the required low pressures, normally between 10^{-1} and 10^{-5} mm. Hg, whereas the drive, heater elements and other essential components of construction are situated in a part of the chamber which can be maintained at a pressure as high as 2–5 mm. Hg.

Z. M. Rybalka & N. Podnik
Brit. Pat. 747,620

Separation of Mixtures by Low-Pressure Rectification

136/III

Russia. The paper is concerned with methods for the separation of thermally unstable organic substances, close in physico-chemical properties, including all compounds of a molecular weight greater than about 150–200. Molecular distillation cannot be used in many of these cases, because the efficiency of most laboratory molecular stills is equivalent only to one theoretical plate, instead of the 10–15 needed. Low pressure operation at a residual pressure of 0.1–3 mm. has previously been shown to be a satisfactory method and this paper describes the development of various methods to obtain data needed for the solution of practical problems. The methods investigated were: (1) Separation with a packed column; (2) separation in a column with hot and cold zones; (3) separation in a column with a rotating cooled-water and a heated casing; (4) separation in columns with rotating rotors, causing turbulence in the vapour and liquid phases. The system studied was dibutylphthalate-dibutylazeleate. The coefficient of relative volatility of this system varied with the composition from 1.14 to 1.48; the b.p. at 1 mm. of the former constituent is 150°C and of the latter 155°C. The results of method (1) showed that: (*a*) Columns with packing of wire spirals 2 and 4 mm. diameter are extremely effective, at atmospheric pressure; (*b*) under reduced pressure both the output and the efficiency are lowered to about $\frac{1}{3}$ to $\frac{1}{5}$ of their values at atmospheric pressure; (*c*) even at low throughputs the pressure drop through the column under reduced pressure is considerable (1.76–3.1 mm. Hg), so that a column with efficient packing can only be used for the separation of substances where vapour pressure is greater than 3–5 mm. and which do not decompose under this condition. In method (2) it was found that (*a*) the separation depends on the amount of heating and cooling and on the rate of flow of vapour through the column but depends very little on the height and number of zones per unit length of column; (*b*) the best separation is attained where the flows of liquid and vapour through the height of the columns are constant; (*c*) a plot of the number of theoretical plates against rate of flow passes through a maximum; (*d*) a column about 1 m. high operating on the above mixture contains the equivalent of 5 theoretical plates and can be used for rectification at a pressure of 0.1–0.8 mm. Hg in the boiler. With method (3) the efficiency of the column depends on the rate of distillation, the amount of heat fed to the jacket and the degree of cooling of the rotor. Under optimum conditions the internal walls of the jacket should be covered with a continuous film of reflux; this was difficult to achieve because the mixture used wets glass badly. Similar details are given regarding method (4).

Report by N. M. Zhavoronkov V. A. Malyusov N. N. Umnik
A.E.R.E. Rep. No. Lib/Trans 694
July 1956

Various Experimental Distillation Methods

137/III

France. The writer describes the experimental methods developed in the last five years at the Etablissements Barbet for the investigation of distillation problems. He surveys successively: The investigation of distillation in glass apparatus in the laboratory, the experiments on pilot columns, and the experiments on full-scale plates, from the fluid mechanics angle. He shows the need to have two pilot columns for half-scale experiments: one for high-temperature vacuum distillation, one for distillations below 150°C. (300°F.) The paper contains a detailed description of these two types of columns: Assembling, heating, control. Under the heading 'extrapolation from half to full scale' the writer surveys the problems met with, the yields of the plates, the engineering of an industrial plate (diameter, shape), and shows why a full-scale testing bench had to be built for the investigation of a number of problems which cannot be solved theoretically. This testing-bench is described, and indications are given on the results obtained.

(*Author*)

Article by Anon.
Gen. Chim. 75, March 1956 60-63

Vacuum Distillation Apparatus

138/III

United States. In the separation of materials by vacuum distillation it is often desirable to obtain true fractionation rather than simple separation. At atmospheric or higher pressures, bubble cap or packed columns can be used; but at lower pressures—*i.e.* for the processing of thermolabile materials—the gas conductances of these devices are too low to be practicable. Hickman designed a column-type of fractionating still consisting of a heated cylindrical outer column with a cooled rotating axial core. Vapours passing up the annular gap were repeatedly condensed on the core and then flung outwards by centrifugal force on to the hot wall. The higher vapour pressure components were readily revaporised and the less volatile components were collected at chosen levels of the column. This design has been further developed by Taylor (*U.S. Pat.* 2,562,153) and the construction described here is based on the latter. It consists of a cylindrical column heated externally by a suitable winding which extends so as to cover all except the uppermost zone. A central rotary condenser, motor-driven and water-cooled, is divided into four zones. Annular gutters, rotating with the core, are placed at the lowest point of each zone and are designed to collect liquid from points immediately above them. The gutters drain into pipes which, rotating with the condenser, conduct the condensate radially outwards and upwards to the next zone. Metal skirts above the ring gutters help to direct the condensate into the latter and also serve to screen pumping apertures from condensate. Liquid enters the still at a point in the lower half of the column and is spread over the heated surface by the action of flexible metal chains which sweep round with the condenser and help to distribute the liquid over this surface in a thin film. By the means described each condensing fraction is advanced to a vaporising point at a higher temperature than it has previously reached and in any given zone the mixture on the outer wall consists of residue from the next higher zone and distillate from the next lower zone. A vertical spacing of 2 inch. between ring gutters has been found to be efficient.

E. S. Perry, D. S. Cox & Eastman Kodak Co.
U.S. Pat. 2,749,292

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Fractionation Process and Apparatus

United States. Fluid mixtures of wide boiling range, such as crude petroleum oil or synthetic crudes, are normally fractionally distilled in columns giving overhead, side and bottom fractions. A temperature difference of 50 to several hundred degrees Farenheit may exist between the top and the bottom of the column, so that the product streams from the lower portions of the column are much hotter than the overhead fraction. This latter is normally partially condensed with normal temperature cooling water and the uncondensed gases treated to recover volatiles by compressing the gasses over another water-cooled condenser. Alternatively, the gases may be condensed by passing them at atmospheric pressure over a condenser cooled by mechanical refrigeration, or operating the whole column under pressure to increase the condensing temperatures of the fractions. The present invention relates to fractional distillation using a refrigerated overhead condenser without vapour recompression. A secondary refrigerant, normally water, boiling under reduced pressure is used to cool this. A solution of a salt such as lithium bromide is used as the working material of an absorption refrigerator which cools this water by absorbing water vapour boiled from it. The diluted salt solution is circulated to a regenerator where it is concentrated using waste heat from the still. The concentrate is returned to the absorbing zone in a closed cycle. The water vapour driven off in the concentration process is condensed and returned for chilling and re-circulation to cool the overhead fraction condenser. The waste heat from this refrigeration cycle may be used to preheat the crude oil feed to the column. The process enables the advantage of the refrigerated condenser to be achieved without the use of expensive compression refrigeration machinery. A steam ejector is used to maintain the vacuum in the water chiller and brine concentrator. The overhead condenser temperature may be lowered from about 85 to 120°F, when normal cooling water is used, to 40 to 50°F when this invention is used. This enables the temperature of the flash section of the distillation column and the crude oil feed to be lowered 50 or 100°F. The invention may be applied not only to primary fractionating columns but to fractionating-column combinations, such as debutanisers and depropanisers, working in series on the overhead fraction of a primary column.

R. L. Irvine
U.S. Pat. 2,742,407

140/III

Integrated Set of Laboratory Fractionators for Routine Analytical Distillations

Canada. A new design for a routine, all-glass laboratory fractionator makes possible precisely controlled 15/5 fractionation. This is achieved using a compact reflux divider, together with the high thermal resistance of a silvered vacuum jacket plus electric compensation. Heat losses are closely controlled, and speed of operation under vacuum is markedly improved. An atmospheric fractionation can be completed in one 8-hour shift. Five sizes of these 15-plate distillation units having capacities ranging from 1 to 80 litres are operating satisfactorily up to 950°F equivalent atmospheric vapour temperature. They have been found ideal for crude oil assays and laboratory workup of refinery operations.

(*Authors*)

Article by G. M. Cooke & B. G. Jameson
Analyt. Chem. 27, Nov. 1955 1798-1802

141/III

The Brush Still. Construction Details and Performance Data

United States. The construction and performance of a brush still are described. In this type of high vacuum still, a rotating central core carries an arrangement of brushes which scrape the walls of the column. In the model described, which had an 11 inch. column 3½ inch. in diameter, the central rotating core could be cooled by either air or water. The core carries a stirrer on its lower end to agitate the liquid in the still pot, and either spiral or flat brushes along its length. A speed of rotation of 450 r.p.m. is convenient and, as speeds of up to 1,800 r.p.m. were tried without any important difference in the results, this speed was adopted for all tests. Nichrome heaters were wound round the outer wall of the column and around the still head condenser. An internal heating element in the boiler was supplied with current through glass-sealed terminals in the pot wall. Heavy magnesia insulation was used on the boiler. The head condenser was a water-cooled double-walled cone, and the condensate could either be sampled for analysis, returned to the boiler, or refluxed down the column. In normal operation, no reflux is used for this type of column, but for experimental work on the determination of the optimum operation conditions, total reflux was employed and a test mixture of 39.5 mole % di-*n*-octyl phthalate and di-2 ethylhexyl sebacate was used. Too little heat to the still resulted in the upper part of the column being dry, too much, caused a drop in performance, but, providing the walls of the column were wetted all the way up, satisfactory separation was achieved with low boiler inputs. Air or water-cooling of the rotating core were almost equally efficient, though at low distillation rates a maximum of 10 theoretical plates was reached with air and only 8 with water-cooling. Strip brushes were tried in place of the spiral brushes normally used. They proved less efficient and, at higher distillation rates, had little effect at all. The still was operated with the distillate being returned to the boiler to simulate the conditions of continuous distillation and it was found that the still could be operated satisfactorily without reflux. For a 150-watt boiler heater and 205-watt column heater input, it is predicted that with a product rate of 60 c.c./hr., a separation of 72.8 mole % of di-*n*-octyl phthalate will be achieved with a 3:1 reflux ratio and 70.6 mole % without reflux during distillation of the test mixture. The theoretical plate values for the column drop rapidly, if the brushes are short and do not touch the column. The pressure drop along spiral brushes exceeds 160 μ Hg if there are 80 bristles to the inch along the spiral. If the number is reduced to 40 to the inch, the pressure drop is reduced without affecting the efficiency. The pumping system employed to evacuate the still consisted of a Consolidated Vacuum Corporation GB-25 oil diffusion pump backed by a 1 litre/sec. displacement mechanical rotary pump. The GB-25 is a two-stage booster type pump. Finally, the performance of the brush still is compared with that of those used by Benner and Byron *et al.*

Article by E. S. Perry & D. S. Cox
Industr. Engng. Chem. 48, Sept. 1956 1473-1478

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The Brush Still. Distillations of High Molecular Weight Organics

142/III

United States. It has been shown previously (*Ind. Eng. Chem.*, **48**, 1473) that the brush still has a relatively high fractionating power, under high vacuum, with low pressure drop. Thus it should be suitable for distilling high molecular weight substances with low thermal hazard. This conclusion was tested by distilling a number of substances in the pressure range from 1 to 6 mm. Hg. The results show that the still can be useful in the moderate pressure range as well as under higher vacua. The still differed a little from that described in the paper quoted above. The boiler was fitted with a 500 watt external heater, the brush shaft was air-cooled and an air-cooled alembic-type product condenser of the kind used on 'boiling point' stills was fitted. The distillations were conducted without the use of reflux in a batchwise manner with just sufficient boiler heat being used to ensure that the column was wetted to the top. Many fractions were taken and these analysed as far as possible. Tall oil, cedarwood oil, peppermint oil, citral, polythylene glycol and ionone were distilled. An account, illustrated with graphs of each distillation, is given of the separation achieved and the nature of the fractions. The performance of the still with ionone compares favourably with that of a 20-theoretical plate spiral screen column of the type described by Stallcup, Fuguitt and Hawkins.

Article by E. S. Perry *Industr. Engng.* **48**, Sept. 1956 1479-1482

Vacuum Distillation of Water On a Laboratory-Scale. Thermal Difference Plant

143/III

United States. The dimineralisation of sea water could be affected by applying the principle of thermal difference, where two sources of different temperatures are available. The use of this principle depends on the exact knowledge of the mechanism of evaporation under vacuum. The authors investigate the various theoretical methods of approach hitherto employed and report on certain observations made experimentally. It is shown that the performance of a low pressure thermal difference plate is largely affected by the liberation of dissolved air, noticeably by bubble formation, which is examined closely. The yields obtained by the authors agree reasonably well with the yields calculated from the Langmuir formula for evaporation from a surface under vacuum. Further, the experiments indicate a relationship between volume of condensate and operation pressure which may have significance for the design of industrial stills of this kind.

Article by L. Akobjanoff & E. D. Howe *Research* June 1956 220-226

Trends in Fatty Acid Distillation

144/III

See Abstract No.: 151/I

On the Basis of Lignite Tar II. The Distillation of Light Oil Bases and the Separation of Some of the Technically Important Pyridines

145/III

Germany. An extensive review is given of previous work concerned with the isolation and identification of individual components constituting lignite tar bases. Details are given of a fractionating column having a high number of theoretical plates and being designed exceptionally compactly. The possibilities of using this column for the separation of a number of technically important pyridine bases has been investigated.

Article by K. Naumann L. E. Leibnitz *Chem. Technik.* **8**, August, 1956 458-471

39 — MISCELLANEOUS PROCESSES — 39

New Idea in Vacuum Cooling

146/III

United States. A mobile vacuum-cooling unit is described mounted on three truck trailers. Two of these carry cooling chambers and the third the vacuum plant. The cooling chambers are cylindrical, 22 feet long and 8 feet in diameter. Each chamber can hold 230 corrugated cartons of 24 heads of lettuce which can be cooled from normal field heat to 42°F in thirty minutes. 34°F can be achieved if required. The third trailer carries an oil-burning Vapor-Clarkson steam generator, the steam raised being used to operate jet pumps capable of producing a 29.8 vacuum in the cooling chambers. The plant which can be taken down in one day and moved and re-assembled in another has been used for large-scale operations in the New York area. Costs are in the neighbourhood of 20 cents per carton of lettuce.

Article by Anon. *Pre Pack Age* **10**, Sept. 1956 4-6

Better Grapefruit Products

147/III

See Abstract No.: 85/III

Irradiation and Antibiotics May Team Up to Preserve Meat

148/III

United States. Abstracts are given of various papers published at the 8th Research Conference of the American Meat Institute. Army tests have shown that dehydrated foods are well accepted by the consumer, and freeze-dehydrated meat is preferred to meat dried by other means. Freeze-dehydrated meat has better storage stability than air or vacuum-dried meat. Its high quality is attributed to the low temperature and high vacuum used in processing. Undesirable flavour and texture changes are avoided and a final moisture content of less

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than 2% can be obtained. Freeze-dehydrated meat must be packed in an oxygen-and-moisture impermeable container to prevent storage deterioration. Its texture and flavour are improved by the addition of certain inorganic ions to the water used for reconstitution. Raw steaks, chops and fish have been prepared for army-user tests. Another paper discussed the use of gamma radiation for destroying bacteria on fresh meat held at near freezing temperatures. Antibiotics such as the tetracyclines improve the shelf life of fresh meat and may prove useful in conjunction with gamma radiation. A further paper described the use of nuclear magnetic resonance as a non-destructive means of measuring the moisture content of hygroscopic foodstuffs. The technique is based on the differences of the magnetic properties of hydrogen atoms in water and in solids such as carbohydrates and proteins. Moisture content is indicated by an electrical signal which can be used for the automatic control of dryers and blenders.

Article by Anon. *Food Engng.* 28, May 1956 57, 178

149/III

Vacuum Container Incorporating a Hand Operated Vacuum Pump

Germany. A small pumping device is described which is fitted to the centre portion of a specially designed metal lid to be used on glass jars of the type normally employed in the food trade and closed at the top by a rubber ring and metal lid. The pump is of the diaphragm type and can be actuated by one finger. The centre of the special lid is pressed to form a frusto-conical casing and has a hole communicating with the interior of the jar. A suitable top plate placed over the casing is used to hold the annular diaphragm made from rubber or plastic in position at its outer edge, whereas in the centre the diaphragm is secured to a knob-like piston moving in the axis of the lid. A return spring brings the piston back to its starting position until the desired vacuum is obtained when the piston remains at the bottom of its stroke. Subsequent deterioration of the vacuum is indicated by the piston returning to the upper position. A shield below the suction valve, prevents any part of the contents of the container from entering the pump. An air-admission valve is provided to facilitate the opening of the jar.

M. Frey *Brit. Pat.* 756,517

150/III

Automatic Vacuum Pan Controls

United States. The production of sugar crystals in a vacuum pan can be automatically governed by four interacting controls which determine the absolute pressure, the steam flow, the crystal growth and the supersaturation of the sugar solution respectively. This development follows the initial use of the supersaturation recorder to indicate the value at which seed should be added to the pan. A throttling butterfly valve regulates the water to the barometric condenser and controls the absolute pressure in the pan. A differential pressure instrument measures the steam flow into the sugar solution. Crystal growth is controlled after grain establishment by measuring the 'tightness' or 'mobility' of the crystalline mass with an agitator paddle. The addition of feed is regulated as a function of this paddle's power consumption or torque. The instrument for controlling super-saturation is a Brown Electronik recorder having two resistance-bulb temperature measuring elements. One bulb is immersed just under the surface of the sugar solution in the downtake of the vacuum pan's calandria. The other is inserted into a pilot pan mounted on the top shoulder of the vacuum pan, near the entrainment separator. This bulb measures the temperature of the condensing vapours. Satisfactory functioning of the supersaturation recorder requires the vacuum to be controlled through the entire run. This is desirable in any case to avoid unstable operation of the pan. During the initial boil-up period the rate at which super-saturation rises is controlled by varying either the pressure or the steam flow. When the seed point is reached a measured amount of seed solution is automatically added to the pan. Absolute pressure or steam flow is then varied to assist the establishment of the grain and then these two variables are kept constant and the rate of crystal growth is regulated by the 'mobility' controller. A master sequence control actuates the separate controls at the appropriate time and allows the pan to be charged, started-up, stopped and dropped automatically. The supersaturation zone can be divided into three areas of increasing concentration; The metastable zone, the intermediate zone and the labile zone. 'Full seeding' in the metastable zone, *i.e.* the addition of nuclei equal in number to the required number of crystals, is the general practice to avoid the formation of unwanted new crystals or 'false grain'. This practice has accentuated the need for measuring and controlling the temperature and absolute pressure and the feed-addition rate.

Article by D. R. Hall *Food Engng.* 27, Oct. 1955 69-71

151/III
H. Prensler & Braunschweigische Maschinenbauanstalt A.G. *German Pat. Appl.* B33384 IV/89e

Heater Elements for Vacuum Apparatus to be Used in Particular in the Sugar Industry

Germany. Details are given of a new design of flat-shaped steam heater elements which facilitates the assembly of a heater body consisting of various compartments, to be inserted as a separated entity in the vacuum chamber of a conventional sugar processing plant.

152/III

Improvements in Methods of Making Vacuum Insulated Cabinets

United States. This invention is concerned with an improved method of constructing vacuum-insulated cabinets in which the space between the inner liner and the outer case contains a compressible filler material to support the walls. In this method of construction, the inner liner is covered with a layer of compressible heat insulating material, such as fibre glass, the insulating material having a thickness exceeding the intended final spacing between the case and liner; for example, a thickness of $\frac{7}{8}$ inch for a final spacing of $\frac{1}{2}$ inch. The insulating material is, at least partially, enclosed in a thin flexible sheath and the assembly is then forced into the outer case,

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causing the case to bulge outwards. The top edges of the liner and case are then temporarily sealed, for example with polyvynil tape, and the space between the liner and case is evacuated. The final sealing is carried out under vacuum, for example, by welding the liner and case along a line just below the top edge. This method of construction, when properly carried out, ensures that the sides of the liner and case are not deformed when the space between them is evacuated, the compressed filler material serving to support the walls at their correct separation.

General Electric Co. *Brit. Pat.* 738,970

High-Temperature Vacuum Furnace for Tensile Testing

153/III

United States. Describes an apparatus to enable wire specimens to be heated *in vacuo* to 1,600°C during tensile tests. It is designed to be used with a particular type of American testing machine (the Instron). The vacuum chamber is made from a vertical Pyrex tube 15 inch. long, 9 inch. diameter and $\frac{1}{8}$ inch thick, closed at the ends by two end plates fitted with rubber gaskets, the whole being held together by four rods with wing nuts. Inside the chamber is the cylindrical tantalum heater, 10 inch. long, $\frac{3}{4}$ inch diameter, made from 0.010 inch material, and surrounded by a molybdenum radiation shield. The heater and shield are supported by cross-members and alumina insulators between two vertical $\frac{1}{2}$ inch. copper rods, which also serve to lead current to the top and bottom of the heater tube. At each end, the heater is clamped by heavy copper jaws, those at the top being carried by flat phosphor-bronze springs to allow for expansion of the heater. The power supply is a 5 kVA mains transformer fed by a variable transformer, 160 A at 12 V being needed to give the maximum temperature of 1,600°C. The wire specimen (tests on W and Mo are referred to) is clamped between the bottom of the vacuum chamber and the load cell of the testing machine, and passes along the axis of the heater tube. A short length 2 inch.-5 inch. near the centre of the hot zone is ground to a reduced section and a platinum-platinum rhodium thermocouple supported close to this part of the specimen. The outer casing of the load cell is connected to the upper end plate by a large sylphon bellows, and a smaller bellows fitted to a flange clamped to the outer casing with a rubber gasket seals the moving part. Difficulties due to overheating of the glass and the gaskets, and to degassing of the ceramics, are mentioned.

Article by E. A. Smith & R. W. Guard *Rev. Sci. Instrum.* **27**, June 1956 386-387

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The Vacuum Concrete Technique

154/III

United Kingdom. Two disadvantages of concrete as a constructional material are its weakness when it has a high water content and the loss of time involved before it can be removed from moulds. Vacuum techniques can be used to overcome these defects. Two methods are used. One incorporates a vacuum mat in the formwork of the mould. An airtight outer cover has beneath it a layer of expanded metal, a fine gauze and finally a sheet of linen in contact with the concrete. On applying the vacuum to the mat, water is drawn out of the concrete and collected in the waste removal tank. Alternatively interval water removers consisting of metal tubes with fine perforations wound over with the filter cloth are inserted in the concrete and pumped as before. These are removed just before setting and the holes left plugged with concrete. Experience in the United States shows that these techniques reduce shrinkage, increase frost resistance and improve the strength due to the final lower cement ratio.

Article by R. J. Salter *The Municipal Journal* 2.3.1956 483

New Waste Paper Recovery Method Developed in Austria

155/III

Austria. A new method of waste-paper recovery is described which is said to eliminate, from any kind of paper, all chemical and physical elements except for cellulose fibres. The cellulose fibres when re-claimed are as good as those obtained directly from wood pulp. The waste paper is put into a vacuum-tight steel container which is evacuated. A dilute solution of chemicals is then injected which, as a result of the reduced pressure, thoroughly penetrates and wets the paper mass. The swollen mass is conveyed to the main disintegrator, in which agitators shake out the foreign particles already loosened in the vacuum container. These particles—glue, resin, or printing inks—are drained into a disposal system, the fibres being carried by the water to a cleaning machine. Finally, in a micro-distintegrator the last traces of foreign particles are removed and the fibre agglomerates are separated. After dehydration, grading and compressing, the dry fibres are shipped to the paper mills where they are added directly to the wood pulp. Kaolin can be recovered separately and mixed with the fibre at the last step prior to the delivery to the paper mills. It is estimated that a recovery mill operating by this method and costing about Doll. 75,000 would produce about 6,000 metric tons of clean, immediately usable cellulose fibres at a cost only 20% above that of the waste paper purchasing price. This represents a saving of about 875,000 cubic feet of wood.

Note by Anon. *World's Paper* 6.10.1955 117

A Remote Vacuum-Operated Pipette Controller

156/III

New Zealand. The article describes a vacuum-operated pipette controller for use with radioactive liquids. It consists of a brass 3-way stopcock, positioned at 45° intervals by a pair of steel balls, two needle valves and a vacuum line. In the 'Fill' position the liquid is drawn into the pipette by connecting the pipette to the vacuum line *via* one of the needle valves which serve to controls the rate of intake. In the 'Slow Drain' position, the pipette is connected to atmosphere *via* the other needle valve which enables the liquid level to be adjusted to the datum mark. In the 'Fast Drain' position the pipette is connected directly to the atmosphere. Interconnecting tubing is of small bore (about $\frac{1}{16}$ inch) to avoid overheating with small pipettes. The device can be used with pipettes ranging in capacity from 0.1 to 50 ml.

Article by E. Wright *Atomics* **7**, Jan. 1956 30-32

Abstract No. and References

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157/III

Electrically Conductive Article

See Abstract No.: 34/III

158/III

A Method of Determining Particle Size of Powders

India. A method is described of determining the mean diameter of particles of powder. The powder is placed in the form of a closely packed plug, in the stem of a 25 c.c. bulb. This contains a wetting liquid. Initially, all air is expelled from the plug by sucking liquid through it using a vacuum line. A negative pressure is then exerted on the plug and the rate of flow of liquid from the bulb through the plug is measured. Both the negative pressure and measurement of flow are accomplished using a mercury U-tube and reservoir system, the plugged bulb being attached by a ground glass joint to one U-tube arm and the flow through the plug being indicated by a rise in mercury level in the other. By measuring the time for a given mercury rise a value of the mean powder diameter is deduced from an expression derived from Poiseuille's equation. Results for several powders of mean particle diameters 0.015 to 0.0005 mm. with benzene and water as wetting liquids showed good agreement. Comparison with various other methods gave values of the same order.

Letter by M. L. Lakhanpal, V. D. Anand & B. R. Puri *Nature* 176, 8.10.1955 692

159/III

Gas Counting Techniques in Biochemistry II.

See Abstract No.: 7/IV

160/III

Improved Methane Proportional Counting Method for Tritium Assay

See Abstract No.: 9/IV

161/III

C^{14} Dating with a Methane Proportional Counter

United States. A method is described for the radio carbon dating of samples containing a fraction of a gram of carbon. This method offers advantages which cannot be obtained with other radio carbon dating procedures. The method used is to prepare carbon dioxide from the sample either by treating carbonate samples with chromatic acid or by combustion of organic materials. This gas is then swept by radon free oxygen into an absorption tube filled with 2N potassium hydroxide and recovered quantitatively with acetic acid. The gas is transferred in a copper bomb to an apparatus in which it can be recirculated over a ruthenium catalyst in the presence of slightly over 4 times its volume of hydrogen. A total gas pressure of about 115 p.s.i. is normally used and the ruthenium catalyst is maintained at 475°C. Even when not in use, the catalyst is maintained, under vacuum, at this temperature to prevent possible contamination. Details of the preparation of the catalyst, which contains 1 to 1.5 grams of ruthenium and lasts for at least six months, are given. The carbon dioxide is converted into methane over this catalyst and, when the reaction is complete, the methane is freed of water vapour by cooling one trap in the conversion apparatus to dry ice temperature and is then frozen out by cooling another trap with liquid nitrogen. A stainless steel bomb is filled with the methane by distillation from the trap under vacuum. Pressures of 800 p.s.i. are normally exerted by the methane in the bomb at room temperature, but it is constructed to carry pressures greatly in excess of this. The gas may then be transferred to the counters. These are demountable, teflon gaskets being used as seals, and are filled to two atmospheres with the gas from the bomb. The counter is operated in the proportional 'beta plateau' region. It is surrounded by one inch of mercury shielding, a ring of anti-coincidence cosmic ray counters and eight inches of iron on all sides. This shielding is normal in radio carbon dating work. A block diagram of the associated electronics is given. Counting is carried out for 24 hours and determinations on modern carbon specimens show that samples 34,000 years old would give a count twice the standard statistical error of the background count for the counters which use a 0.85 gram sample. Those counters using a 0.22 gram sample will be affected in the same way by a sample 26,000 years old. Larger samples and reduced background counts could lead to higher accuracies and greater measurable ages.

Article by W. H. Burke & W. G. Meinschein *Rev. Sci. Instrum.* 26, Dec. 1955 1137-1140

162/III Report by W. J. Arrol E. J. Wilson & C. Evans *A.E.R.E. Rep. No.* I/R.1135 April 1953

The Routine Production or Zirconium-Tritium and Zirconium-Deuterium Targets

United Kingdom. The preparation is described in some detail of targets of zirconium evaporated on to metal backings and impregnated with deuterium or tritium. Thickness of zirconium varies between 150 and 1,200 μg./cm.^{2} and the atomic ratio of hydrogen isotope to zirconium is usually 1:1 and at best 1.5:1.

(*Authors*)

163/III

Helium-Cooled Liquid Hydrogen-Deuterium Target

United States. A target chamber 4 inch. in diameter and 5 inch. high has hydrogen or deuterium condensed into it from the gaseous phase by the boil-off vapour from liquid helium. The walls are of 0.00075 inch thick stainless steel and are surrounded by a 0.001 inch aluminium foil, liquid nitrogen cooled, radiation shield. A description of the method of fabricating these thin walled target cells is given. A vacuum jacket encloses the whole assembly and the gamma-ray beam enters and leaves through 4-inch. diameter and 0.0015 inch Be-Cu foil windows soft soldered across the end of arms in this jacket. The nitrogen bath which cools the radiation shield and pre-cools hydrogen or deuterium gas entering the cell is surrounded by a separate vacuum jacket. 0.01-inch

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Teflon sheet gaskets have been found satisfactory down to liquid nitrogen temperatures for vacuum sealing. Helium is boiled off from a Dewar flask beneath the target cell, both by the heat leakage in the Dewar and by dissipating 2 watts in a resistor, to fill the cell. When the cell is full, the current is switched off and natural heat leakage suffices to keep equilibrium. A system of microswitches on the hydrogen gasometer guards against overfilling the chamber by by-passing some of the helium gas. The level of liquid helium is determined by using three carbon resistors disposed vertically above one another. These take different currents when immersed in liquid of gaseous helium, if a fixed voltage is applied to them. A stripped 500 ohm $\frac{1}{2}$-watt carbon resistor is also used to measure directly when the hydrogen cell is full. Hydrogen or deuterium is emptied from the cell by allowing a small amount of helium into the vacuum surrounding the target cell. The target has been in continuous operation for six months and has shown itself to be reliable and easily controlled. The thickness of the target is 0.63 g./cm.^{2} or 0.008 radiation lengths on a $Z(Z+1)$ basis with hydrogen, 1.58 g./cm.^{2} or 0.010 radiation lengths with deuterium and the aluminium and stainless steel walls provide a total of 0.071 g./cm.^{2} or 0.0026 radiation lengths.

Article by G. S. Janes, L. G. Hyman & C. J. Strumski *Rev. Sci. Instrum.* **27**, July 1956 527-530

Tritium Gas Target for Neutron Production

164/III

United States. This paper reports a self-contained tritium gas target including beam collimator, target cell, and gas reservoir which has been used for the production of neutrons from the T (d,n) He^4 and T (p,n) He^3 reactions. Beam collimators are 0.14-inch tantalum apertures aligned in precision 1-inch tubing to assure accurate beam measurement. The gas cell is $\frac{5}{16}$-inch diam. and may be any length less than 3 inch. The target window is a 0.00005-inch nickel foil soldered on a $\frac{1}{4}$-inch i.d. re-entrant tube. Tritium is supplied from a uranium-tritide oven; hydrogen-tritium exchange is minimised by the use of nonhydrogenous materials. A discussion is given of handling tritium. The target will tolerate a 1 μamp beam of 2-Mev deutrons for several days without foil damage.

(*Authors*)

C. H. Johnson & H. E. Barta *Rev. Sci. Instrum.* **27**, March 1956 132-134

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The Thermal Conductivity of Bismuth Telluride

165/III

United Kingdom. In this investigation the thermal conductivity of bismuth telluride was measured in the range of temperature 150°K to 300°K. The apparatus consisted of an insulated Nichrome coil embedded in a copper block, the power supplied being calculated from current and voltage measurements. The specimens were of square cross-section and were ground flat and parallel, electro-plated and soldered into position to ensure good thermal contact. The heat sink consisted of a copper cylinder within which slid a copper block which was soldered to the bottom of the specimen. The temperature of the heat source and sink were measured by copper-constantan thermocouples. Control of the temperature of the sink was obtained by varying the degree of vacuum in the space which separated it from an outer cylinder immersed in liquid air, and by adjusting the current flowing in an auxiliary heating coil. Measurements on a number of specimens showed that relatively pure specimens have an inferior heat conductivity at low temperatures compared with specimens containing a significant amount of impurity but that the opposite is true at room temperature, even though the impure samples still have an appreciably greater electrical conductivity. This is explained by supposing that at the lowest temperatures the normal electronic component of thermal conductivity predominates for all specimens, so that those with the higher electrical conductivity (the impure specimens) also have the higher thermal conductivity. At room temperature, however, the intrinsic carrier concentration is greater for the pure specimens and the consequent transport of ionisation energy down the temperature gradient is sufficient to raise the thermal conductivity of the pure specimens, above that of the impure specimens. This explanation is confirmed quantitatively by the results of the investigation.

Article by H. J. Goldsmid *Proc. Phys. Soc.* **69B**, Feb. 1956 203-209

Method of Degassing Liquids

166/III

United States. A method for the degassing of liquids or recovery of gases from liquids is described which was developed in work where the quantitative recovery of small amounts of gas (a few micromoles) was hindered by the presence of air in the liquids involved. Essentially the apparatus consists of a low-temperature reflux condenser in which the liquid can be refluxed under vacuum at a temperature where its vapour pressure is negligible (<1 mm). Liquids having high vapour pressures above their m.p., such as water and benzene, are excluded unless they are combined with a previously degassed liquid of lower boiling point to form a low-melting eutectic. Details of the arrangements are given. Degassing of the liquid is accomplished by refluxing using a dry-ice-trichloroethylene slurry in the condenser and a liquid nitrogen trap. Magnetic stirring of the liquid aids degassing in the initial stages and pumping is continued until the pressure in the system is less than 1 micron Hg. The vacuum pump is then isolated, the dry ice removed from the condensers and the liquid distilled into receivers which are subsequently sealed off *in situ*. The system for the quantitative recovery of dissolved gases from liquids is essentially the same. An additional stop is necessary, however, in order to recover high boiling gases such as butanes. The non-condensable gases are removed by a Toepler pump and the condensable gases are cut into as many fractions as desired by liquid nitrogen pumping across a series of traps. Results obtained when various gases were added to degassed isopropyl ether are given in a table. Application to pure solvents with high vapour pressure at their melting points—*e.g.* benzene—is only possible in combination when another previously degassed solvent of lower boiling point is present to form a low-melting mixture with the high melting solvent in question.

Paper by A. S. Newton *Anlyt. Chem.* **28**, July 1956 1214-1215

Conditioning Plant for Steam Turbine Lubricating Oils

167/III

United Kingdom. Contamination of steam turbine oils still occurs, though not on the scale that it once did, and Menrow Limited have conducted research at a number of power stations to overcome this. Equipment has been developed and is now being manufactured under O. E. Nekolla's patents using a new approach to the problem. Oil from the main turbine reservoir is delivered to a de-aerator-separator in which it flows upwards over a series

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of baffles. The gross water contamination falls to the bottom and air bubbles rise to the surface. The oil now passes to a precipitator, in which water present in the form of an unstable emulsion is split off, and thence, if water contamination is high and there are no inhibitors present, through a heater to a vacuum dryer working at a vacuum of about 29.5 inch. If contamination is not serious or inhibitors are present, a preferential surface tension dehydrator is used. In this the remaining water is removed by a non-absorbent material contained in replaceable cartridges. The oil flow is so valved that it can be diverted to each of two cartridges to give continuous extraction. Following dehydration, the oil is progressively chilled to cause deterioration products to separate out in a spongy form and is then passed through a twin Auto-Klean strainer to remove the coarse solid particles. Two filter presses are finally used to filter out the spongy agglomerated impurities and polish the oil to provide brightness. Filter mats are normally used but specially designed grid adaptor plates can be made to ensure that filter aid powders can be safely employed even whilst the plant is operating in by-pass with a working turbine. Choice of the exact equipment required can only be made after a careful study of the particular oil used and its contamination. Analysis of these contaminants at Battersea power station resulted in the location of parts which were wearing. In this case equipment was fitted to give progressively higher degrees of conditioning. The result of adding each cleaning stage is shown diagrammatically. In particular, the reduction in the gum dissolved in the oil is thought to have given improved governor action. The output from the equipment averaged 450 gal/hr. and the total quantity of oil to be treated was 4,200 gal.

Article by Anon.
Mech. World
Aug. 1956
354-356

IV — Special Subsidiary Subjects — IV

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40 — GASES AND VAPOURS — 40

Adsorption of Gases on a Silicon Surface 1/IV

United States. The adsorption of argon, nitrogen, carbon dioxide, carbon monoxide, hydrogen, oxygen and water vapour on a silicon surface has been examined using a mass spectrometer and a flash filament technique. Measurements were made at 300°K (room temperature) and at gas pressures between 10^{-7} and 10^{-4} mm. Hg. The decomposition of carbon dioxide and water vapour at various temperatures has also been studied. A filament was cut from a silicon crystal, etched and mounted in a glass tube. This tube could be evacuated through the ionisation chamber of a mass spectrometer from which the inlet leak had been removed. Molybdenum leads were soldered to the ends of the filament to carry the heating current, and temperatures within the range of visible radiation were determined with an optical pyrometer. The silicon filament was first outgassed for several days in the best vacuum attainable in the system (about 10^{-8} mm.). Adsorption of argon, nitrogen, hydrogen, carbon monoxide, carbon dioxide and water was tested as follows: The filament was flashed several times to 1,200° *in vacuo* and the gas was then introduced into the tube while the filament was cold. After varying time intervals, and with the gas still flowing, the filament was flashed. During the run the spectrometer was focussed on the mass of an ion fragment of the gas, and the gas desorbed was measured on the recording oscillograph. At the same time, as a check, the change in pressure in the tube was read on an ion gauge. To test the reversibility of the isotherm, the gas could be pumped out before flashing the filament. In the pressure range 10^{-7}–10^{-4} mm. Hg the change in pressure on flashing was between 10^{-6} and 10^{-5} mm. Hg. In cases where reaction occurred, as in the decomposition of water and carbon dioxide, the spectrometer was focussed on an ion fragment of one of the reaction products with the gas flowing through the system and the filament cold. The silicon was then heated in steps of 100 or 50° and a continuous record was obtained of the partial pressure of the decomposition product. Adsorbed oxygen cannot be determined by flashing the filament since it comes off as silicon oxide which is not sufficiently volatile to reach the ionisation chamber. In this case the silicon was flashed in a high vacuum and allowed to cool. Oxygen was admitted and pressure-time curve was plotted. At the end of the run the system was evacuated with the filament remaining cold. Oxygen was then re-admitted and a second pressure-time curve was plotted. The first curve shows adsorption and the second does not. If steps are taken to prevent adsorption on the glass apparatus, a comparison of the two curves provides a measure of the adsorption of oxygen on silicon. The experiments indicate that at 300°K and at pressures below 10^{-4} mm. Hg, argon, nitrogen and carbon monoxide are not adsorbed: Hydrogen and carbon monoxide are adsorbed without reaction. When carbon dioxide was passed over the filament, heated above 800°, decomposition occurred to carbon monoxide and, presumably, an oxide of silicon. In the case of oxygen almost every oxygen molecule striking the filament was adsorbed until the first oxide layer was formed. The 'sticking probability' then decreased as further oxide layers were built up. A monolayer of oxygen was adsorbed on silicon at pressures near 10^{-6} mm. The heat of adsorption of oxygen on silicon was calculated to be 173 kcal./mole. When the filament was flashed after the adsorption of water vapour, most of the gas desorbed was hydrogen, twice as much hydrogen being desorbed as after the adsorption of molecular hydrogen.

Paper by J. T. Law & E. E. Francois *J. Phys. Chem.* 60, March 1956 353-358

Study of the Absorption in Km Waves of Gases Adsorbed by Silica Gel or Titanium Oxide 2/IV

See Abstract No.: 77/II

Multilayer Adsorption on Plane Surfaces by Capacity Measurements I. Adsorption on Glass at High Relative Pressures 3/IV

See Abstract No.: 78/II

The Adsorption of Some Organic Vapours by Wool and Nylon 4/IV

United Kingdom. The literature gives some information about the penetration of nylon and wool by non-solvents in the liquid phase, but less about the mechanism of absorption in the vapour phase, and this chiefly concerns water vapour. Work has now been done on the adsorption of organic vapours. A McBain and Bakr spring balance was used. The reagents were enclosed in a sealed glass capsule in a tube (liquid reservoirs) and could be released by dropping a steel ballbearing. The vapour reservoir was connected to a Barr and Stroud 2-stage, high vacuum, lens coating unit. The balance spring was made of Pyrex glass, annealed for 8 hours at 200°C. The apparatus was evacuated to a pressure of 10^{-4} mm. Hg. For low temperature experiments, it was enclosed in an air thermostat. For high temperatures, the adsorption tube was immersed in a thermostatically-controlled paraffin oil bath with the reagent reservoir outside so that it could be heated independently to a higher temperature than the bath to accelerate vapour production. The bath was of copper, with a Pyrex glass window for observing the spring; oil was circulated through a copper coil. Preliminary adsorption tests on nylon and wool were conducted with hydroxylic compound: acetic acid, ethanol, ethylene glycol, methanol, phenol, *n*-propanol and water, and with various non-hydroxylic compounds. The former showed concentrations of adsorbate of >1600, >550, 380, >1450, >1150, >510, and >1750 m-mol./Kg. respectively, whereas the latter showed nil-260, only aniline and dioxan showing any appreciable adsorption. Data for adsorption-desorption rates are given. In a comparison of ethanol, methanol and water, the rates of both adsorption and desorption of nylon increased in the order of decreasing molecular size: ethanol < methanol < water. The whole of the adsorbed methanol could be desorbed. The isotherms for the three vapours demonstrate that methanol and water

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are absorbed by nylon to the same extent, but wool adsorbs less methanol than water. Both nylon and wool adsorb ethanol less readily than methanol. Isotherms for methanol vapour and water vapour on nylon are almost identical. The maximum amount adsorbed is 1 mole/kg. for both. Curves for adsorption rates of methanol vapour on wool are shown. At saturation v.p., adsorption rises to 8 moles/kg., equivalent to 65% of the total amount of polar groups in wool, i.e., peptide, hydroxyl, and amino and free acidic groups in the side-chains. If the whole of this adsorbate is present as a monolayer in amorphous parts of the fibre, 23% of the fibre must be inaccessible to the methanol molecule. To test the possible effect of traces of moisture on the adsorption of hydrophilic vapours, the rate of adsorption on wool of intensively dried glacial acetic acid was compared with that of the normally dried acid and found to be much lower, adsorption on dry wool of hydrogen chloride gas was barely measurable. Rate curves of phenol vapour on wool at 25°, 60° 70° and 80°C and on nylon at 25°C are shown. On nylon there was a slight discontinuity in the curves at 25° at 0.94 mole/kg. On the assumption that phenol mols. are attached to each amide group this is equivalent to 5.3% of the total number in the fibre. Accessibility of the amorphous regions is therefore lower than with methanol but the high affinity of phenol ensures rapid penetration of the crystalline regions. Neither nylon nor wool suffers damage at temperatures up to 150° for as long as 8 hours at a pressure of 10^{-4} mm. Hg. Adsorption experiments could therefore be conducted with alizarin, benzoic acid, and β-naphthol at temperatures up to 140°C. A striking increase in adsorption capacity of both nylon and wool in successive cycles of adsorption and desorption was revealed. It may be attributed to a progressive breakdown of the crystal structure of the fibres by disruption of internal hydrogen bonds and their replacement by new attachments to the bulky molecules of the absorbate. The energies of activation of vapours calculated from the initial slopes of the rate curves are tabulated.

Article by
H. R. Chipalkatti, V. B. Chipalkatti & C. H. Giles
J. Soc. Dyers & Colourists
71, Nov. 1955
652-660

5/IV

Semiconductivity and Catalysts in the Nickel Oxide System

See Abstract No.: 156/I

6/IV

The Surface Areas of Evaporated Metal Films

See Abstract No.: 55/III

7/IV

Gas Counting Techniques in Biochemistry II.

United Kingdom. The determination of tritium is discussed in samples prepared from biochemical specimens as described in Part I of the article. The tritium can be determined as water vapour or an hydrogen, but in either case the counters become contaminated to an inconvenient extent and the author prefers to prepare an organic vapour or gas from the specimen. This can be readily manipulated with the aid of liquid air traps—another disadvantage of hydrogen is that it cannot. The gas recommended by the author is butane, prepared from the radioactive water by treatment with a Grignard reagent. The reaction tubes used hold about 13 ml. and are connected to the apparatus by a cone joint and a vacuum stopcock—silicone vacuum grease is used. Six tubes are prepared at a time: 1.5 ml. of a 2N solution of *n*-butyl magnesium bromide in dry ether is pipetted into each and the ether then removed on the rough vacuum line by distilling-over into a trap cooled by liquid air. Remaining traces of ether are removed by baking the tubes on the high vacuum line at 120°C for 1 hr. and the labelled water is then sublimed into a reaction tube—about 10 mg. can be handled. The tube is then again heated to 120°C for 1 hr. after which the stopcock is opened and the butane driven off to condense in a tube adjacent to the counter; any unreacted water is intercepted by a U-tube chilled by solid CO_2. The butane is divided into two or more samples in separate tubes isolated by stopcocks and each then admitted to the stainless steel counter at a pressure of 12.5 cm. Hg. The counter then works at about 2.4 kV. The specific activities of the samples should agree to within 1.5%. Some examples of the application of the gas-counting technique in biochemistry are briefly discussed; The cheapness of using tritium to label a fatty acid (*e.g.*) rather than a carbon isotope, is emphasised. Tritium is readily obtainable with a high specific activity. A further advantage of the techniques described is that several experiments can be made at once, by using several isotopes; for example, tritium, C^{13} and C^{14} can be used to label different parts of a molecule and then assayed independently.

Article by
R. F. Glascock
Atomics
6, Dec. 1955
363-369

8/IV

The Determination of Tritium in Tritiated Water

Article by
A. Finkelstein & M. Lesimple
J. Nuclear Energy
2, Dec. 1955
101-109

France. A simple determination of tritium in tritiated water has been developed, using the reaction of tritiated water on calcium carbide, and counting the acetylene formed in a calibrated ionisation chamber. No memory effects have been observed; a slight isotopic separation was detected and estimated.

(*Authors*)

9/IV

Improved Methane Proportional Counting Method for Tritium Assay

Article by
C. V. Robinson
Nucleonics
13, Nov. 1955
90-91

United States. An improved form of tritium assay by means of a metal including methane generation and proportional counting reported previously is described. In the new version a metal system can be used. The method includes reaction of a labelled aqueous sample with a methyl Grignard reagent to generate labelled methane, purification, transfer of the gas into a counting chamber and operation of the chamber as a proportional counter. A 0.2 ml. sample is required and 8 ml. of $IMCH_3MgI$ dissolved in butyl ether. The efficiency of the method is 11%. Details of the equipment and operational procedure are given.

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New Isotope Separation Process Pushed in Germany

10/IV

United States. Reference is made to work reported by Becker, Bier and Burghoff (*Z. Naturf.* **10A** No. 7, 1955) on separation of argon and xenon which promises to become a suitable method for separation of U^{235}, cheaper and simpler than gaseous diffusion. The mixture of gases is fed into a pipe with a DeLaval nozzle outlet opposite a cone-chaped paring tube. The gap between the two can be varied. Lighter component gas tends to accumulate near the edges of the stream issuing from the nozzle, is pared off by the separator and collects in an upper chamber. Heavier component tends to collect at centre of stream and passes to a lower chamber. The outlets from the two chambers are attached through valves to mercury vapour diffusion pumps. The gas samples are drawn off on the fore vacuum side of pressure of 12 mm. Hg maximum. Becker has shown that the capacity of apparatus can be considerably increased by using flattened rather than round nozzles and separators. A 0.2 mm. wide, 20 mm. long nozzle gave separations like that with 0.5 mm. diameter round nozzle yet has 12× the throughput. Cascade apparatus with recycling of depleted gas is envisaged. Replacement of barriers in gaseous diffusion process by separation nozzles leads to greater reliability and substantially higher output for the same cost.

Note by Anon. *Nucleonics* **14**, June 1956 19A

On the Origin of Atmospheric Argon

11/IV

Belgium. Most of the radiogenic argon took part in the formation of the atmosphere in the period preceding the time at which differentiation of the mantle and crust was sufficiently accomplished. Argon was one of the first constituents of the terrestrial atmosphere and has acted from the very beginning as a screen for x-rays and ultraviolet radiations at wavelengths less than 800 Å.

(*Author*)

Article by M. Nicolet *Bull. Classe Sci.* **42**, No. 4 1956 482-505

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Anode Temperature and Characteristics of the d.c. Arc in Noble Gases

12/IV

See Abstract No.: 58/I

Ultra-violet Absorption of Atomic Nitrogen in its Ionisation Continuum

13/IV

United States. Knowledge of the absorption cross-section of gases is important in the study of gas discharges, of ionospheric layers and of stellar atmospheres. Since in many cases the absorbing gas is ionised, excited or dissociated, it was thought useful to compare the absorption in a column of neutral gas with that in the same gas excited by an electric discharge. This was done by passing radiation through the plasma in a Philips Ionisation Gauge (P.I.G.) into a normal incidence vacuum spectrograph. The region 400–800 Å was recorded photographically on calibrated plates. The spark source consisted of a 2 mm. bore tube of zirconium dioxide and two Al electrodes and was excited by discharging a capacitor, charged to 20 kV, periodically by means of a motor-driven rotary switch. The radiation from the end of this capillary passed axially down the P.I.G. which had a discharge path 58 cm. long, with a perforated anode and cathode at each end. The P.I.G. discharge was run at 30 mA from a 3 kV d.c. supply, with an axial field of 2,000 gauss. The light source and the P.I.G. were electrically and magnetically shielded from each other and small magnets were placed at the source exit slit to stop charged particles from the P.I.G. entering the source. After passing along the P.I.G. tube, the radiation fell on a concave grating of 50 cm. radius of curvature and having 30,000 lines per inch, and the spectrum was received on a u.v.-sensitised film, 2 inch. × 10 inch. (Eastman, 103–0). The three parts of the apparatus were separately pumped, the source running at 0.1 mm. Hg of air and the P.I.G. at 0.02 mm. of nitrogen. After several minutes running, an exposure would be made with the P.I.G. turned off, a second with the gauge on and a third, as a check, with it off again. The film would then be calibrated. With a micro-densitometer, the intensity ratios of each spectral line were determined, but ignoring those source lines which coincided with a P.I.G. emission line. Assuming Lambert's law of absorption, the difference between the logs of the intensities with and without the discharge running is shown to be proportional to the difference between the absorption cross-section for molecular N_2 (no discharge) and the composite cross-section for all the particles in the plasma. Known data for the cross-section of N_2 were then used to calculate that for the plasma. The results show an overall spread of $\pm 20\%$, with a maximum cross-section at about 650 Å ,and general agreement with the theoretical results of Bates and Seaton. The results are interpreted by considering the various possible mechanisms of absorption in N_2, N, $N^\dagger$, N^*, and metastable atoms and molecules. The difference between the absorption in the neutral and ionised gases was found to be almost independent of λ (range studied 400–700 Å), which was taken to indicate an absorption continuum. Consideration of the ionisation energies of the various possible photo-ionisation processes leads to the conclusion that absorption by neutral, atomic nitrogen was responsible. To obtain an estimate of the percentage of atomic N in the P.I.G. discharge, the energies required for the possible mechanisms of ionisation by electron collision are examined and hence the probabilities of the different ionisation and dissociation reactions are estimated. Trial calculations to give a self-consistent set of percentages of the different components are shown and it is concluded that the plasma composition is probably: N_2—60%, ($N^\dagger_2$+$N^\dagger$)— 15%, N— 25%. The absorption cross-section for the atomic N was then calculated. To eliminate possibilities of the absorption continuum being spurious, subsidiary tests were performed by varying the P.I.G. discharge current, switching on and off the magnetic field, and by applying various potentials to one pair of P.I.G. electrodes without an actual discharge. Finally, there is considered the possibility that a change in temperature or pressure when the discharge is switched on might cause the effective absorbing path length, which is reduced to N.T.P., to be different for the two exposures. A separate series of experiments is described, in which the P.I.G. discharge was interrupted at the same frequency as the spark, so that the discharge was switched off

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Article by A. W. Ehler & G. L. Weissler *J. Opt. Soc. Amer.* **45**, Dec. 1955 1035-1043

for a short time before and after each spark. Various time delays were tried and it is concluded that no ions, excited or metastable states existed in the P.I.G. discharge 0.1 millisecond after switching off, so that the absorption observed must be due to atomic or molecular nitrogen. The absorption did not vary measurably for time delays up to 5 millisec., consistent with known values of the recombination coefficient of atomic N. The final value for the absorption cross-section of atomic N is given as 12.8×10^{-18} sq. cm.

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Negative Hydrogen Ion Source

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Negative Hydrogen Ion Source

See Abstract No.: 54/IV

16/IV

'Glo-Ball' Development

See Abstract No.: 49/IV

17/IV

Space Charge and Ionisation Phenomena in Constant-Gradient Proton Synchrotron

See Abstract No.: 50/IV

18/IV

Flow of Gases Through Packed Bed of Silica Powder at Low Pressures

United Kingdom. The authors investigated the permeation of hydrogen, helium, air and Freon vapours through a bed of silica powder of a grain size of 4×10^{-6} cm. and specific surface area of 100 m.²/g. at pressures ranging from 0–10 micron Hg. The resistance to flow is evaluated in terms of 'specific conductance (K)', which is the conductance of l.c.c. of the powder

$$K = \frac{CL}{At} \text{ (cm.}^2\text{/sec.)}$$

where C is flow rate/pressure drop, L is bed-length, A is bed cross-section area and t is time. The results are presented in graphs and show that the relationship between specific conductance and gas pressure is linear down to a certain pressure value below which conditions are no longer consistent. Air and Freon show an increase in specific conductance at zero pressure, whereas the other two (lighter) gases show the opposite. This indicates the presence of a new flow mechanism which is related only to molecular weight of the gas and not to its mean free path. The authors conclude with a brief discussion of the experimental results.

Article by A. G. Monroe & D. I. Gaffee *Nature* **178**, 28.7.1956 197-198

19/IV

High-Speed Rotating Cylinder for Rarefied Gas Dynamics Research

See Abstract No.: 18/I

41 — FREEZE DRYING — 41

20/IV

Freeze-Drying I. Introduction

United Kingdom. Heat-sensitive biological materials are widely dried by sublimation from the frozen state to avoid changes which occur if they are dried by other means. The dried material is sponge-like and suffers no volume reduction during drying. It is said to be 'lyophile', *i.e.* very easily rehydrated. Freeze drying is an expensive process and may sometimes be replaced by methods involving high temperatures for only short times without great loss in quality of the product. Many materials may also be preserved merely by storage in the frozen state, but, as they can be stored, when dry, at room temperature in a suitable package, the dried material is more convenient. The theory of freeze drying is simple. If the pressure over a frozen sample is reduced below the saturation vapour pressure of water at the temperature of the sample, water will evaporate from it. Latent heat must be supplied to maintain evaporation and this may be effected by conduction or radiation. The lower the temperature of the material, the lower the pressure that is required. For drying at −40°C an oil-sealed mechanical rotary pump may be used to produce a satisfactory vacuum. Most difficulties occur in supplying the latent heat of evaporation and removing the water vapour. To make the whole apparatus independent of refrigeration, the evaporative freezing technique of Greaves was used. In evaporative freezing, the removal of heat of evaporation from the liquid state is used to produce cooling. The liquids tend to froth and either controlled outgassing or centrifuging during freezing is used to overcome this. Chemical dessicants such as phosphorous pentoxide or silica gel are employed. The latter, however, has a low absorption unless it is refri-

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gerated. Direct pumping of the vapour by rotary pumps equipped with oil clarifiers, or by steam ejectors, has been employed, but all these systems have been superseded for all except small laboratory units by traps cooled by mechanical refrigeration. Continuous condensers, either using scrapers to remove the ice from a cold surface, or using a cold salt solution into which the water vapour condenses, sprayed into the chamber, have been designed in order to utilise the advantages offered by a continuous, as opposed to a batch, drying process. For large-scale drying, manifold systems are cumbersome and the vessels containing the material to be dried are either placed on heated thermostatically controlled shelves or individually into heated cans inside evacuable chambers. Freezing of 400 c.c. quantities of blood products on a large scale was achieved by Greaves by rotating the bottles rapidly about a vertical axis in a cold air stream. The material was spread around the sides of the bottle and froze with a large surface area. Though problems related to drying plant have been largely solved, difficulties relating to the optimum final moisture content and suspending media for living organisms remain.

Article by R. J. C. Harris *Lab. Practice* 5, Jan. 1956 5-7

Freeze-Drying II. Small Scale Freeze Drying in the Laboratory

21/IV

United Kingdom. The instability which is a characteristic of many biological materials is increased by a rise of temperature, water acting as the catalyst. Freezing will often inhibit degenerative processes in the materials, but temperatures lower than the eutectic temperatures of any salts present are required. The troubles associated with low temperature storage makes freeze drying an attractive method of preservation, and, although much complex apparatus is available, useful drying can be done by simple means in the laboratory. If water is evaporated from the liquid phase of the material the concentration of salts and protein can result in irreversible changes known as denaturation. This concentration does not occur during drying from the frozen state. Though the water vapour evolved in drying can be directly pumped by certain vacuum pumps or trapped by refrigerated surfaces, a desiccant trap filled with, say, phosphorous pentoxide, about 17 c.c. of which are required for 1 ml. of material, will be found most economical. The passage of vapour between the frozen material and the desiccant should be as unobstructed as possible. If, as is recommended, a vacuum desiccator is used to hold the material and desiccant, any narrow bore glass tap fitted should be removed and a $\frac{1}{4}$ inch bore pump line and a gauge connection fitted in its place. Amounts of material greater than 1 ml. may be outgassed by successive short applications of low pressure and then snap-frozen by self-evaporation. Quantities below 1 c.c. should not be treated in this way, as the amount of liquid evaporating to cause freezing gives rise to excessive concentration of the material, with consequent denaturation. Although the vacuum pump, theoretically, may be switched off after a pressure of 0.1 mm. Hg or better has been achieved, experience shows that there is a slow outgassing of the material during drying, so it is safer to leave it running. Bottles with screw closures should be avoided, as their rubber washers are permeable to water. Fry and Greaves have suggested a fluid consisting of three parts serum and one part broth with 7.5 grams of glucose added to every 100 ml. as suitable for suspending micro-organisms for drying. This liquid is liable to froth when dried by the method given above and a serum-glucose mixture, though it gives a lower survival rate, dries better. A mixture of 20% bovine albumin and 5% glucose in water has the advantage that there is no chance of agglutination of the organisms. The glucose in the media retains some water and prevents over-drying of organisms with consequent loss of viability.

Article by R. I. N. Greaves *Lab. Practice* 5, Feb. 1956 53-55

Notes on the Lyophilisation Technique

22/IV

United States. A large number of biochemistry laboratory courses do not include practical demonstrations of the freeze drying technique. A simple, inexpensive easy-to-operate apparatus suitable for the purpose is described and illustrated in the present note. The condenser flask of the glass apparatus is supported by crushed solid dry ice and acetone placed in a Dewar vessel. As the carbon dioxide sublimes the condenser is gradually lowered into the vessel. Fitted with a one-litre flask the apparatus will remove 850 ml. of water in 24 hours of uninterrupted operation.

Note by A. W. Devor E. B. Titchener, C. E. Andre & W. J. Frajola *J. Chem. Educ.* 33, 1956 343

The Micro-Determination of Residual Moisture in Freeze-Dried Biological Materials

23/IV

See Abstract No.: 168/I

Freeze-Drying III. The Preservation of Micro-Organisms

24/IV

United Kingdom. Micro-organisms are preserved in the living state for convenience and uniformity and to avoid the necessity of sub-culturing or animal passage. For preservation the water and/or oxygen activity is reduced by freezing, drying or maintaining cultures under paraffin oil. Freezing, usually in a dry-ice cabinet at about −80°C, is widely used for preserving viruses. The method is not so extensively used for bacteria, though it is capable of preserving some bacteria which so far have not been satisfactorily dried. Hog mucin and glycerol additions have been used to protect bacteria, spermatozoa and trichomonads during freezing and the method may be capable of dealing with protozoa and algae. It is necessary to protect the material frozen from absorbing carbon dioxide from the high concentrations present in the freezer. Dried preparations have the advantage of stability at room temperature, but many of the methods used for drying in the past were unnecessarily complicated. On the assumption that, at least with some suspending media, it is unnecessary to freeze before drying and that only sufficient material need be dried to preserve the culture, a small glass manifold drier has been developed. Water vapour is absorbed in a phosphorus pentoxide trap. Glass ampoules contining one drop of material each are connected *via* rubber nipples to glass stopcocks mounted on the manifold. When

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the ampoule of material is attached and the apparatus evacuated the material forms froth. A cotton wool plug in the neck of the ampoule prevents any material being expelled. Drying is complete in an hour and the ampoules are then removed, necked, re-evacuated and sealed under vacuum. Difficulties in opening the sealed ampoules are minimised if the procedure used by the National Collection of Type Cultures is employed. The serum-glucose mixture recommended by Greaves in the previous article in this series and a peptone-glucose mixture used by the author are suitable as suspending media for the bacteria. In a great deal of the past work on the preservation of bacteria, surfaces other than the glass walls of the tube have been used to support the material during drying. Fibrous or granular material provides a larger surface area, for rapid drying. The author has dried some difficult organisms from the viscous product resulting from incorporating a bacterial suspension in a small plug of freeze-dried peptone. For larger quantities of material, freeze drying, either using the evaporative freezing method of Greaves or pre-freezing the product, is necessary. Many animal viruses, moulded and bacteriophages have been successfully dried and Becquerel has shown the drying of protozoa and algae to be possible.

Article by D. I. Annear *Lab. Practice* 5, March 1956 102-105

25/IV

Maintenance of Yeasts by Freeze Drying

United Kingdom. Earlier work has shown that the vast majority of yeast cultures which have been freeze-dried survived the process, but very few cells of any one culture remained viable. The vitamin requirements of these survivors frequently differed from the parent cells so, before adopting freeze drying as the sole method of preservation in the National Collection of Yeast cultures, tests were conducted for up to two years on the viability, fermentation reactions and vitamin requirements of 83 freeze-dried yeast cultures from 12 genera. The initial work and the results after nine months storage are reported. 0.1 c.c. of the cultures, which had been grown for two successive occasions on a medium (MYGP) consisting of malt extract, yeast extract glucose and peptone, was mixed with 0.1 c.c. of a modified 'Mist. desiccans' medium containing 7.5% glucose in horse serum in a sterile ampoule. Freeze drying was carried out in an Edwards's Model 2A freeze drier. After drying, the ampoules were sealed under vacuum and stored in the dark at approximately 0.5°C. The viability was determined immediately before, 2 days after, and 9 months after drying. Any ampoules that showed marked loss of vacuum when examined with a high frequency tester were rejected. To determine the initial viability, 0.1 c.c. of the culture was added to 0.9 c.c. of sterile water and 5 drops of a series of ten-fold dilutions of this mixture were placed on MYGP agar plates previously kept at 40°C and now stored at 25°C. Drops from which 10–25 colonies developed in 24 or 48 hours were counted. The procedure for freeze-dried cultures was similar except that 1 c.c. of liquid was added to the ampoule to give an initial 1:10 dilution. The results indicate that, though there were wide variations in survival both between genera and between species in any genera, there was an average viability of 8.6% after 2 days storage and 7.6% after 9 months. *Brettanomyces* survived very badly, so a different suspending medium is probably required for this genus. The fermentation reactions investigated using a the micro-fermentation technique of E. O. Morris and Kirsop (*J. Inst. Brew.*, 1953, 486) showed no changes after treatment or storage. The vitamin requirements of 28 strains of *Saccharomyces*, however, when investigated by a modification of the method of Schultz and Atkin, (*Arch. Biochem.*, **14**, 369) in which readings were taken over longer periods than usual, showed differences after treatment and storage. Usually the ability to synthesise vitamins was increased. It was shown that growing a yeast in a vitamin-deficient medium for 24 or 28 hours does not give a satisfactory picture of the growth rate. Yeasts may either grow at the same rate as in a vitamin-rich medium, grow slowly but at a steady rate, grow slowly or not at all at first and then suddenly develop at the normal rate, or not grow at all. These differences are not clearly distinguished by the test and the conclusion is drawn that it has only limited taxonomic applications. The stability of vitamin requirements of cultures stored under normal conditions must be further investigated before any conclusions can be drawn as to the effect of freeze drying on these properties.

Article by B. Kirsop *J. Inst. Brewing* 61, Nov.-Dec. 1955 466-471

26/IV

What is a Virus?

See Abstract No.: 172/I

27/IV

Electron Microscope Observations of Periodicities in the Surface Structure of Tobacco Mosaic Virus

See Abstract No.: 63/II

28/IV

Fine Structure of Tobacco Mosaic Virus

See Abstract No.: 64/II

29/IV

Freeze-Dried B.C.G. Vaccine. Methods Adopted in Preparation of a Standard Product

United Kingdom. During the past thirty years, in which B.C.G. vaccine has become widely established as an effective agent against tuberculosis, liquid vaccines have been principally used. The discovery that freeze drying could preserve living bacteria led to attempts to produce a dried vaccine. Such a vaccine should (*1*) contain a sufficient number of viable antigenic organisms, (*2*) be relatively free from organisms producing marked reactions, (*3*) be stable at normal temperatures, (*4*) be pharmaceutically elegant and easy to reconstitute and (*5*) be dried in a material which does not cause unpleasant side reactions on injection. Several attempts made to produce such a vaccine failed in one or more of these aspects. In particular, most vaccines were grown

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as surface cultures and the harvested pellicle was ground in a ball mill. This resulted in clumping of the material making viability counts difficult and causing reactions when the vaccine is subcutaneously injected. The milling may also damage the cells themselves. The present paper describes the production of an improved freeze-dried B.C.G. vaccine. The Copenhagen substrain of the B.C.G. strain was used as a starting point. This was freeze-dried at the commencement of the work and regular recoveries made from this master culture at three monthly intervals. The submaster cultures are carried through three transfers at 7 day intervals in Dubos liquid medium. The third culture is inocculated on to Sauton's medium to which the important addition of 1/4000 w/v of 'triton WR 1339' wetting agent is made. This agent is not affected by, nor does it affect, the culture but eliminates clumping of the growing culture and makes deep culturing of the B.C.G. possible. The thickness of the layer of Sauton's medium (8 mm.) and the temperature (37°C) are critical. After 9 days, the cultures, which grow as a layer on the bottom of the culture flask, are agitated gently to form a uniform suspension consisting of single cells with a few small aggregates of up to 10 cells. The cells are harvested by centrifuging below 10°C for 30 minutes at approximately 2,500 g. and are resuspended in an aqueous medium containing 8.3% dextran and 7.5% glucose. 0.5 c.c. of this suspension which contains 1 mg. moist weight of B.C.G. is filled into each 2 ml. ampoule for freeze drying. The ampoules are pre-frozen in a shelf freezer at −50°C and dried in a specially adapted freeze drier for sixteen hours. The ampoules then have their necks constructed, are further dried for four hours over phosphorous pentoxide and are finally sealed under vacuum. Moisture measurements have been made on the dried vaccine by both a vapour pressure method and the Karl-Fischer Method. Viable cells in the material are estimated using O'Hea's modification (*J. Path. Bact.* **69,** 169) of the method of Miles *et al.* (*J. Hyg. (Camb.)*, **38,** 732). Tests on guinea pigs were made to assess the absence of virulence, the degree of reaction to the vaccine and tuberculin conversion. Viability counts on different ampoules from any one batch did not differ by more than the experimental error. Tables, partly reproduced below, show the effects of storage time, glucose concentration and storage temperature on the vaccine. A direct relationship between the viable cell counts and the size of local lesions after intradermal injection in guinea pigs has been found.

Relation Between Storage at 20°C. and the Viability of the Freeze-dried Vaccine

Time After Preparation	*Viable-cell Count per ml Reconstituted Vaccine**		
	Batch A	*Batch B*	*Batch C*
0	1.5×10^6	115×10^6	0.5×10^6
1 month	Not tested	Not tested	0.28×10^6
3 months	2.6×10^6	95×10^6	0.2×10^6
9 months	Not tested	75×10^6	0.2×10^6

* Average of two ampoules enumerated separately, each count duplicated.

Relation Between Glucose Concentration in the Medium, Residual Moisture, and Viable-Cell Count.

Batch	*Composition of Drying Medium*		*Residual Moisture Content*	*Viable-cell Count per ml. Reconstituted Vaccine*
	Dextran	*Glucose*		
Z1	8.3%	20%	Unsatisfactory product*	
Z3	8.3%	7.5%	1.26%	10.0×10^6
Z5	8.3%	1%	0.20%	0.02×10^6

* Medium containing 20 % glucose and thawed out during the later stages of freeze-drying to give a 'boiled toffee-like' solid of ugly appearance.

Article by J. Ungar, P. Farmer & P. W. Muggleton *Brit. Med. J.* 8.9.1956 568-571

Freeze-Dried B.C.G. Vaccination of Newborn Infants with a British Vaccine 30/IV

See Abstract No.: 174/I

Carzinophilin 31/IV

See Abstract No.: 175/I

Canine Distemper—Immunisation with Avianised Virus 32/IV

South Africa. Canine distemper is not a disease confined to dogs. Ferrets, mink, weasels, ermine, marten, raccoon, wolf, fox and jackal are known to be susceptible. A review of earlier work on the aetiology of the disease and the production of vaccines against it is given and the production and properties of an egg-adapted vaccine from the Ondestepoort Laboratory described. The starting material for vaccine production at Onderstepoort was a sample of ferret origin canine distemper vaccine produced by Green's method. This was reconstituted and injected into two ferrets. One of these suffered a marked febrile reaction. It was killed and its spleen

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suspended in broth with a Waring blendor. The supernatent fluid produced by centrifuging was seeded into the chorioallentoic membranes of developing chick embryos, using the method of Alexander (*Onderstepoort J.*, **2**, 9 and *Ibid.*, **22**, 7, 1947). The eggs came from a flock of White Leghorns free of bacillary white diarrhoea. The eggs were then re-incubated at 35°C as this temperature was found to give the highest yield of virus growth with the least number of embryo deaths. Propagation of the virus by injection by the yolk-sac, allantoic and amniotic routes was unsuccessful. Freshly harvested chorio-allantoic membranes were macerated with an equal volume of 2% peptone and 10% lactose in M/25 phosphate buffer at pH 7.4 and then lightly centrifuged to give a supernatent fluid which was dried in 0.5 ml. amounts in a centrifugal freeze dryer. Ampoules were sealed under dry nitrogen and stored at minus 15°C for maximum stability. A table showing the keeping qualities of the dried vaccine is reproduced below. The wet vaccine had an unstable potency after 24 hours storage at 32°.

Keeping Qualities of Freeze-dried Onderstepoort Virus Preparations

Batch No.	*Vehicle.*	*Sealed Under*	*Stored At*	*Time in Days.*	*Dilution Injected into Ferrets.*							
					10^{-1}		10^{-2}		10^{-3}		10^{-4}	
					A.	*B.*	*A.*	*B.*	*A.*	*B.*	*A.*	*B.*
2	Aq.dist...	Air...	−15°C	81	I	I	I	I	I	I	—	—
			37°C	7	NI	NI	NI	NI	NI	NI	—	—
23	Aq.dist...	Nitrogen	−15°C	8	—	—	I	I	I	I	—	—
			37°C	7	I	NI	I	NI	I	NI	—	—
37	Aq.dist...	Nitrogen	−15°C	16	I	I	I	I	I	I	NI	NI
			37°C	7	I	I	I	NI	NI	NI	—	—
93	Lactospep-tone buffer	Nitrogen	−15°C	17	—	—	—	I	I	I	I	I
			37°C	7	—	—	I	I	I	I	I	I

Note I — Immune to homologous challenge
NI — Not immune.

By the 130th egg passage the virus was satisfactory for producing immunity in ferrets and dogs safely. When this was found to be so, large scale tests were made on dogs. During the last three years, 40,000 doses of the vaccine have been issued. Usually no visible reactions are noticed on inoculation, but a slight febrile reaction from the fourth to the eighth day afterwards has been found and occasionally dogs are listless during or after this reaction. Dogs and ferrets immunised with the Onderstepoort virus were challenged with distemper viruses obtained from early serial egg passage and from locally occurring cases. A solid immunity was found to have been produced in all cases. In the titration of the vaccine in eggs and ferrets, lesions were found to be produced in eggs at dilutions down to 10^{-4} whilst ferrets and dogs required innoculation at a dilution of not greater than 10^{-2} to give immunity. However it was concluded that a vaccine giving a well defined lesion in an egg would confer immunity in dogs and ferrets. The majority of failures reported with inoculations of Onderstepoort vaccine showed central nervous system involvement. The diagnosis of several canine diseases is difficult and, though it is believed that the majority of cases diagnosed as encephalitis are caused by distemper virus, there is some doubt as to whether all the strains of virus isolated from cases of canine encephalitis are the same as the classical distemper virus. It has become apparent that some artificially or naturally immunised dogs are liable to develop the encephalitic form of distemper.

Paper by
D. A. Haig
Onderstepoort J. Vet. Res.
27, Jan. 1956
19-53

33/IV

Purine Compounds in Snake Venoms

See Abstract No.: 53/I

34/IV

Freeze-Drying IV. The Preservation of Tissues

United Kingdom. Much biological work today depends on close analysis of cell structure and composition. The century-old techniques of fixing in formalin or other solution, dehydrating by washing in alcohol and then embedding in paraffin wax is still used but often presents the worker with a mere 'caricature' of the original living cell tissue. Freezing and drying from the frozen state was first applied to this problem by Altmann in 1890. About 1930, Gersh reinvestigated and improved this method and from this time onwards steady development has taken place. It is well known that if a solution of protein and salt is frozen, ice crystals will separate and the dissolved matter will be precipitated at crystal boundaries. To obtain a really true picture of the distribution of this dissolved matter, the smallest possible ice crystals are required. Crystals of 1 μ or less are obtained by freezing in liquid nitrogen using a heat-transfer liquid such as isopentane or propane to avoid the slower cooling that would occur if the tissue were immersed directly in the liquid gas and covered by gaseous nitrogen bubbles during freezing. As isopentane and propane are dangerous when mixed with liquid oxygen, dichlorodifluoromethane should be used instead, where the latter coolant has to be used. Layers of material should not be more than 1 mm. thick for good freezing and the frozen material should never be allowed to rise above minus 30°C as harmful re-arrangements in the crystal structure may occur. A compromise drying

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temperature of −30 to −50°C is chosen as ultra-low temperature desiccation would take an inconveniently long time. Three designs of tissue dryer are described and the close proximity required between the evaporating and condensing surfaces is emphasised. Embedding in paraffin wax may be accomplished either inside or outside the dryer immediately after desiccation and sections may be cut from the paraffin block in the usual way. However, because the tissue has not been fixed, the normal procedure after sectioning has to be modified and reagents used which render the constituents insoluble without altering the structure. Often these solutions are analysed after use to see what they have extracted from the tissue. If it is not possible to build or construct a tissue freeze dryer, it is possible to enjoy some of the advantages of frozen and dried tissues by freezing the material as described and then extracting the water by washing in methyl alcohol at −60°C. Cold dry nitrogen may also be passed over the frozen tissue to effect drying. Artery and bone grafting material is freeze-dried *in vitro*. This is used by the surgeon to fill gaps in bones or arteries to guide the growth of new tissue into the wound.

Article by L. G. E. Bell *Lab. Practice* 5, April 1956 139-142

Improved Freeze-Drying and Embedding Apparatus for Frozen Tissues

35/IV

United States. The apparatus consists of an evacuated drying tube immersed in a solid CO_2-alcohol mixture. Although a mechanical fore pump would produce a sufficiently low vacuum in this tube, a diffusion pump and mechanical backing pump combination is used to get a rapid pump down and higher speeds at 1×10^{-4} mm. Hg. A central stainless steel rod in the drying tube supports a cup, at its lower end, filled with embedding wax which has been previously outgassed for an hour, while molten, under the vacuum of the mechanical fore pump. Immersed in this wax are a heater and thermocouple. The tissue sections, which have been previously frozen in isopentane cooled by liquid nitrogen, are placed in $\frac{7}{16}$ inch wide by $\frac{5}{16}$ inch high baskets resting on this wax. Drying is effected by applying heat from the heater in the parafin wax and, at the end of drying, the Variac control to the heater is turned up to melt the wax and embed the sample. A Teflon insert in the support tube allows certain flexibility in the drying head when it is being placed in the drying tube and also thermally insulates the head from conduction down the support tube. Baffles mounted on the support tube direct the water vapour to the cooled walls and thus protect the pumping system from contamination. Two Pirani gauge heads are fitted to the unit, one near the mechanical pump and the other near the tissue. The difference between the readings of these can be taken as an indication of the progress of the early stages of drying.

Article by E. W. Emmart & L. R. Crisp *Rev. Sci. Instrum.* 27, May 1956 315-318

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A Simple Apparatus for Freeze Drying Historical Specimens

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Australia. The construction and operation of a simple apparatus for freezing-drying historical specimens is described. The apparatus, which is constructed from materials readily available in most laboratories, requires neither elaborate pumping equipment nor vapour traps, for the water molecules emanating from the specimens are carried away by a stream of dry gas. By this means specimens can be dried from a lower temperature in a time considerably shorter than is possible with the more complicated and costly freezing-drying apparatus usually used.

(*Authors.*)

Article by H. Kramer & R. G. Hill *Guard. J. Microsc. Sci.* 97, Sept. 1956 313-317

An Experimental Comparison of Freeze-Dried and Frozen Cortical Bone-Graft Healing

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See Abstract No.: 170/I

Freeze-Drying V. Freeze Drying as a Large-Scale Operation

38/IV

United Kingdom. Freeze drying provides a technique for preserving biological materials which enables them to be distributed by normal methods of transport and stored for long period without deterioration. It has been extensively used for blood plasma and serum and makes transfusion possible at places a long distance from the blood bank. Transfusion materials are best dried in the bottles in which they will be used. These are usually of half to one litre capacity. Other materials are dried in small quantities, in ampoules, and special plant has been developed to handle these. Blood plasma was first dried on a large scale in this country in a plant, designed by Greaves, which differs little from its modern counterparts. In this, 400 c.c. blood plasma are filled into a transfusion bottle and a porous cap fitted to maintain sterility during drying but permitting the escape of water vapour. The bottle is then left in a cold room to cool to 4°C and then spun-frozen by the vertical spin-freezing method of Greaves. As an alternative to this procedure, shell freezing in a cold liquid bath or vertical spin-freezing using a liquid coolant may be employed. The bottles, after freezing, are transferred to the drying chamber. This can take many forms, but a mechanically refrigerated condenser is normally employed together with a rotary vacuum pump for roughing and either a diffusion and rotary pump combination or a smaller rotary pump for holding the vacuum. Steam ejector pumps are not economic unless cheap process steam is avilable. Electrically heated cans around the bottles usually provide the heat of evaporation, but water heating has been used in America and water vapour heating in a manifold dryer in Holland. After this primary drying, during which 98% of the water is removed, the bottles are vacuum dried at room temperature over P_2O_5 and then vacuum-packed at a moisture content, well below 1% of the dry weight. This drying procedure is described fully with reference to the plasma dryer due to Kekwick (1945) and constructed by J. &. Hall Limited. Ampoule drying can be undertaken in a similar desiccator to plasma drying, but the drying head must be adapted to take a very large number of small containers. These containers are frozen by self-evaporation, using centrifuging to prevent frothing, or by circulating a cold liquid through the plates on which they stand. The heat for evaporation may be provided by passing warmed liquids through the trays or by electrical radiant-heating. Secondary drying over P_2O_5 is also used for complete drying of these materials. Finally, mention is made of the drying of fibrinogen foam in bulk.

Article by L. Vallet *Lab. Practice* 5, May 1956 169-173

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39/IV	**Preservation of Animals and Plants by Drying from the Frozen State** *United Kingdom.* Owing to the inadequacy of methods at present being used, the preservation of whole animals and plants for exhibition has been attempted by freeze drying. Hard-bodied insects can be vacuum-dried without pre-freezing, but soft-bodied insects cannot be so treated. Even if they do not burst during evacuation, they shrivel during drying. The rate of evaporation from animals that live in water is sufficient to maintain them in the frozen state during drying. However, a layer of mucous substances over slugs and earthworms dries to give an opaque white surface which cannot satisfactorily be wiped off. Caterpillars, the colour of which is contributed to from within, such as some green species, loose colour on freeze drying; other caterpillars do not and dry satisfactorily, taking up no more than 2% of water when exposed to the atmosphere and remaining hard, but slightly flexible, to the touch, They have been stored under atmospheric conditions satisfactorily for over a year. Quick freezing is necessary to avoid the formation of large ice crystals which give a more fragile product and specimens are normally frozen in solid CO_2. Spiders are difficult to freeze because of their high fat content and must be soaked overnight in trichloroethylene. After freezing, specimens are allowed to warm to $-15°C$ in an ice box, for drying. With larger specimens, the increased volume-to-surface area ratio means that drying is prolonged. A pipistrelle bat and a mouse weighing 18 g. have been dried, though the latter animal took three weeks to desiccate. Fungi are beautifully preserved by this technique. 90% of their weight is lost in drying, the largest loss recorded, and 2% of water is re-absorbed under normal laboratory atmospheric conditions. Migratory locusts lost the least weight during drying (50–54%). Although no deterioration has been detected after storing any specimens preserved by freeze drying, it might be wise to inject a non-volatile disinfectant, before freezing, into those which are required for permanent collections. Article by D. A. L. Davies & V. S. G. Baugh *Nature* 177, 7.4.1956 657-658
40/IV	**Irradiation and Antibiotics May Team up to Preserve Meat** See Abstract No.: 148/III
41/IV	**Drying of Fruit Juices by Freeze Drying** *France.* The author surveys briefly known methods of preparing powders from fruit juice by freeze drying and concludes that, while the quality of the products is generally excellent, processing procedures are too costly to permit production on a commercial scale. This is, essentially, due to the fact that all methods are typical batch production methods. The aim is to devise satisfactory continuous processing procedures. The author reports on a series of experimental freeze drying operations with that aim in view, processing a large variety of fruits first on a pilot scale (1952–1954) and finally on a semi-industrial scale. Article by P. Dupaigne *Fruits* 11, Jan. 1956 25-30
	45 — ELECTRONICS — 45
42/IV	**Use of Krypton-85 in Measuring Gas Clean-Up Rates** See Abstract No.: 8/I
43/IV	**Origin and Analysis of Gas in Electron Tubes** *United States.* Observation of the gas pressure in an electron tube during cathode conversion and subsequent anode heating showed that gas is given off by the cathode and adsorbed by the anode. Mass spectrographic analysis of the gas, after taking suitable precautions to minimise background effects, showed that the gas given off by the cathode and adsorbed by the anode is carbon dioxide. This gas then reacts with barium given off by the cathode to form carbon monoxide which is emitted when the anode is heated or subject to electron bombardment. The adsorbed gas is not successfully dealt with by a getter owing to the large amounts involved. A suitable solution is to keep the anode hot (above 600°C) during cathode conversion and subsequent pumping off of the carbon dioxide. During the experiments pressures of about 10^{-5} mm. Hg were used, obtained by diffusion pump aggregate. A Westinghouse metal vacuum valve was placed between the tube and pumps to control pumping speed. An ionisation gauge was situated between the tube and the valve, and a cold trap between valve and pumps. Article by S. J. Stoll *Brit. J. Appl. Phys.* 7, March 1956 94-96
44/IV	**Some New Thermionic Cathodes** *United Kingdom.* Thermionic cathodes should have the following properties,—(a) high current density of thermionic current per watt of heating power, (b) a low operating temperature, (c) long operational life, (d) ability to withstand bombardment, (e) stability in high electric fields, (f) not easily to be poisoned, (g) capable of accurate fabrication, (h) resistance to mechanical and thermal shocks, (i) not to evaporate Ba or BaO to other electrodes. Existing cathodes do not fulfill these requirements fully. The most common type (the oxide-coated cathode) which is usually a mixture of barium and strontium on a base of nickel, is the most efficient but its deficiencies are becoming more pronounced as vacuum tube technique advances. Higher powers, high

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frequencies, higher electrostatic fields operate against these cathodes which do not possess sufficient mechanical strength and surface regularity. Since the basic materials of the oxide cathode (the alkaline earths) appear to be the most satisfactory emitters, it has been attempted recently to devise cathodes using these materials but eliminating the major disadvantages associated with the conventional designs. One such development is the 'L' cathode which is described by H. J. Lemmens, M. J. Jenson and R. Loosjes, (*Philips Tech. Rev.*, **11**, 341). The L-cathodes have low electrical resistance, great mechanical strength and a smooth surface which may be machined. They also withstand electron bombardment and recover quickly from the effects of poisoning and ion bombardment. Venema (*Le Vide*, **9**, 267) describes some applications of L-cathodes including a disc triode with cathode-grid spacing of 0.04 mm. It has been stated that L-cathodes have lives greater than 8,000 hours when operated at 950°C (brightness) and with an emission density of 1.3 A./cm^2. In another cathode development an impregnated W disc is used instead of the oxide pellet and sintered disc of the L-cathode. R. Levi (*Le Vide*, **9**, 284) uses a sintered mixture of W and barium aluminates giving cathodes which can be machined to close tolerances. D. MacNair, R. T. Lynch and N. B. Hannay (*J. Appl. Phys.*, **24**, 1335) use moulded cathodes made by compressing mixtures of nickel powder and alkaline earth carbonates in steel dies. After sintering the cathodes can be machined as desired. These cathodes are highly resistant to poisoning, stable at high voltages and have emission characteristics between sprayed oxide and L-cathodes. A further form of cathode has been described by W. Balas, J. Dempsey, and E. F. Rexer (*J. Appl. Phys.* **26**, 1163, Sept. 1955) in which sintered nickel is impregnated with a strong solution of barium and strontium acetates in water, followed by a solution of ammonium carbonate to precipitate the carbonates in the pores. These cathodes give emission densities of about 10 A./cm.^{2} and have a work function of about 1.0–1.25 eV.

Article by F. A. Vick *Sci. Progr.* No. 173, Oct. 1955 65-71

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Initiation of Hot-Cathode Discharges

45/IV

United Kingdom. An experimental study has been made of the effect of a voltage fall along a hot cathode on the initiation of a gas discharge in a diode at low pressure. Plasma forms first near the negative end of the cathode and spreads along the cathode with increase in tube current. Positive ions diffuse in the inter-electrode space towards the positive end of the cathode, where the potential difference between cathode and anode when plasma is present may be well below the ionisation potential of the gas. Observations have been made on the appearance of the discharge before and after plasma forms, and on oscillations generated by the discharge.

(*Authors*)

Article by N. A. Daly & K. G. Emeleus *Brit. J. Appl. Phys.* 6, Oct. 1955 370-372

Improvements i.o.r.t. Coating Metals with Composite Metallic Aluminium Compounds

46/IV

Germany. It is known practice to use Al-coated Ni, Fe, etc., to make anodes of radio valves; the metal is coated with Al by rolling after which on heating to a high temperature an intermetallic compound is formed which has good heat-radiating properties. A difficulty is that spots of impurities form on the outer surface, causing hot spots and spoiling the vacuum in the finished valve. The invention describes a modification in which the heating is adjusted so that the intermetallic compound is formed thinly at the interface and the remaining Al is then dissolved away to expose the compound. It is claimed that the surface has a darker colour when formed in this way and that because of the reduced heating the base metal is less affected. An example is described of the treatment of Ni sheet: The sheet is coated with a layer of Al 10 micron thick and then heated for 10 min. at 600°C to form the compound $NiAl_3$. The unconverted Al can then be removed by a weak solution of caustic soda, sodium carbonate or hydrochloric acid, or alternatively by amalgamation with mercury or a mercury salt.

Telefunken G.m.b.H. *Brit. Pat.* 750,637

The Breakdown of Gases Subject to Crossed Electric Fields

47/IV

United Kingdom. The hypothesis is made that in ultra-high frequency breakdown where the drift movement imposed on an electron by the field is very restricted, the localisation of the electron contributes to breakdown. An experimental system is described in which an auxiliary unidirectional or relatively low-frequency field is imposed at right angles to a microwave field to destroy the localisation. When the auxiliary field is unidirectional, or of relatively low frequency (0.86 Mc/s) its application raises the breakdown stress, but when the frequency is raised to 9.7 Mc/s the two fields appear to act quite independently in producing breakdown. A partial explanation is advanced. The gases studied include air, oxygen, nitrogen, hydrogen and neon.

(*Authors*)

Article by W. A. Prowse & P. E. Lane *Proc. Phys. Soc.* 69B, Jan. 1956 33-46

Some Factors Influencing Field Emission and the Fowler-Nordheim Law

48/IV

United Kingdom. Investigations of field emission up to fields of approximately 7×10^7 V cm.$^{-1}$ show that the experimentally observed currents tend to be progressively less than that predicted by the Fowler-Nordheim law in the region between 10^7 V cm.$^{-1}$ and 7×10^7 V cm.$^{-1}$. The author does not disagree with the view that these departures from theory are due to space charge distortion of the electric field but draws attention to other second-order effects which may produce departures from the law at higher fields. The Fowler-Nordheim law was established on the assumption that it was legitimate to use the image law and that the field is uniform over distances of the order of 1.0 Å from the surface. The author points out that it has been indicated that it is unlikely that the image law holds within 3 Å of the surface and that since the surface barrier is reduced as the field is increased it is unlikely, in the range up to 7×10^7 V cm.$^{-1}$, that the surface barrier would be like that deduced using the image law. As a result the usual Fowler-Nordheim linear plot would be modified to lower currents in the high field range. This has been ascertained using clean tungsten emitters and also using tungsten

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emitters on which a layer of barium has been deposited to give a range of work functions. The effect being more marked and occurring at lower values of field as the work function is reduced. A slight up-bending of the curve of ln (current density) against the reciprocal of field at higher fields is explained on the basis of non-uniformity of the work function of the surface. The author calculates the order of effect for a clean tungsten emitter having work functions of 4.35 and 4.65 corresponding to different crystal faces and observes that the effect does not depend on the geometry of the emitter. The effect of irregularities on the surface micro-geometry is then discussed. Such irregularities exist, of atomic dimensions, even after flashing of the surface. An investigation of the effect of these on the current-field relationship is pursued and the results show an increase in emitted current over that expected from the Fowler-Nordheim law at high fields. The departures from the normal law therefore fall into two categories associated with firstly nature and uniformity of surface barrier and secondly distortions of the applied field near the emitter. In the former category the failure of the image law is the more serious discrepancy. In the latter category the distortion produced by space-charges has been adequately treated by others and the distortion due to irregularities of atomic dimensions in the surface, discussed in this paper, are in qualitative agreement with experiment.

Article by T. J. Lewis *Proc. Phys. Soc.* **68B**, Nov. 1955 938-943

49/IV

'Glo-Ball' Development

United States. Investigations of electric field distribution in cavity resonators are conveniently made by use of a 'glo-ball'. This device is a small, thin-walled, partially evacuated glass sphere containing helium, which ionises or 'fires' with the emission of light, at a given potential. Although the use of the glo-ball is well established, factors associated with the production of the glo-ball have not previously been determined. The work reported has determined these factors, and data is given to show how various gases, pressures, diameters and frequencies are related to the firing of the glo-ball. Investigations were carried out on glo-balls blown from 10 mm. glass or quartz tubing. Experiments could be carried out with the balls still connected to a manifold, or after sealing and suspending with nylon thread. They were placed in a 1 inch parallel-plate gap, and examination of their characteristics made by increasing the field strength. When the ball 'fired', the modulation cycle was cut off by means of a photomultiplier tube and the maximum voltage automatically recorded. No major differences in electrical behaviour were found using balls made from quartz, Vycor, Pyrex or uranium glass. Quartz and Vycor could stand red-hot temperatures under vacuum, but were difficult to blow. Pyrex was principally used. The simplest method of sealing was by acetylene torch, which introduced some impurities, however. Helium was the best of all gases used for filling the balls. Balls of $\frac{1}{4}$ inch to $\frac{7}{8}$ inch diameter were examined at pressures between 200 μ to 300 mm. Hg. The $\frac{1}{2}$ inch diameter ball is most useful. At low pressures, the gradient necessary for firing changes rapidly with pressure, showing a hump at about 3 mm. and a minimum at about 8 mm. Hg. With increasing pressure, at frequencies of 10–70 Mc., the firing gradient shows an upward and almost linear trend. The firing gradient was generally 200 V/inch., regardless of ball-size. The most satisfactory sealing-off pressure for the $\frac{1}{2}$ inch glo-ball was 10 mm. Firing was inconsistent at the characteristic voltage gradient for a normal glo-ball, in a purely random fashion. No definite improvement in firing stability was found after 24 hours outgassing at 10^{-4} mm. Hg just below Pyrex softening point. Satisfactory stability (2%) was obtained by internal washing of the balls with 10–20% HF solution, followed by 30 mins., outgassing, then sealing. Spectroscopic analysis of the light emitted on firing showed that the stable HF-treated balls had a comparatively high CO_2 content. This suggests that addition of CO_2 may enhance stability. The effects of electrostatic charge were investigated, but were not found to be significant in the problem of firing stability. Characteristics of balls kept for one year showed little change. The temperature of the glo-ball had little effect, generally, on the firing gradient.

Article by J. F. Steinhaus *Rev. Sci. Instrum.* **27**, Aug. 1956 575-580

50/IV

Space Charge and Ionisation Phenomena in Constant-Gradient Proton Synchrotron

United Kingdom. Considerations of the forces on charged particles in a constant gradient proton-synchrotron lead to an expression for the maximum number of particles which can be stably held in the beam, owing to space charge effects. If ionisation of residual gas occurs the electrons at first oscillate, the positive ions being lost to the walls, but when bunching occurs the electrons are rapidly lost to the walls also. The electrons therefore do not neutralise the space charge. Thermionically produced electrons could be used to do this. Data on space-charge reduction by the introduction of thermionic electrons, applicable to the Birmingham machine, is given.

Article by P. B. Moon *Proc. Phys. Soc.* **69A**, Feb. 1956 153-156

51/IV

The Diffusion of Protons Through the Residual Gas in a Synchrotron I. Scattering

See Abstract No.: 119/I

52/IV

A Generator for Fast Neutrons

Holland. Fast neutrons may be produced by the so-called D-D reaction:

$$ {}_1D^2 + {}_1D^2 \rightarrow {}_2He^3 + {}_0n^1 + 3.28\ MeV $$

In the generator described, deuterons ions are accelerated and impinge on a target of heavy ice. Acceleration is achieved by means of a cascade generator consisting of condensers and high voltage rectifiers. It is arranged in three columns around a porcelain tube in which the ions are accelerated. The ions are produced by a discharge in low pressure deuterium gas, maintained by a high frequency alternating voltage. Selenium rectifiers are used, avoiding the necessity for supplying heater current. Nitrogen at a pressure of 10 atm. insulates the generator

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system (which operates up to 1 MV) and the acceleration tube is evacuated by means of diffusion pumps. The target consists of a hollow copper plate with a thin layer (20 μ) of heavy ice on its surface. The ice temperature must be kept below −100°C for otherwise its vapour pressure is too high. The hollow plate therefore contains some liquid nitrogen which evaporates and provides cooling. To reduce local heating the ion beam traces Lissajous figures on the target, which is also rotated. A flux of 10^{10} neutrons per second can be obtained for many hours, at energies up to 4 MeV.

Article by A. C. van Dorsten *Philips Tech. Rev.* **17**, Oct. 1955 109-111

Negative Hydrogen Ion Source 53/IV

United States. An r.f. ion source of conventional type is shown to yield a current of 2.2. μA of negative hydrogen ions. This is accomplished by charge exchange of the positive ions emerging from the plasma with the neutral gas in the probe channel. The negative ion beam is well focused, and the performance of the source is 0.22 μA/c.c. at NTP/hour. The differential equations for the above charge exchange process are set down and solved and found to be consistent with the observations to within an order of magnitude using published cross-sections. The theory also predicts a sizeable neutral beam (∼60 μA) of energy 2–3 kev. According to the equations and the published positive ion performance of these sources, many times larger negative hydrogen ion yields should be obtainable if required.

(*Authors*)

Article by J. A. Phillips & J. L. Tuck *Rev. Sci. Instrum.* **27**, Feb. 1956 97-98

Negative Hydrogen Ion Source 54/IV

United States. The energy of protons accelerated by an electrostatic generator can be doubled if negative hydrogen ions are accelerated to an electrode at a high positive potential, stripped to protons by a thin target in the electrode and accelerated to earth potential. This also has the advantage of allowing equipment at present housed in a high voltage electrode to be kept at earth potential. A source has been developed to provide a suitable negative hydrogen ion beam. A stream of positive hydrogen ions produced in a magnetic ion source, similar in principle to that described by Kistemaker *et al.* in 1950, is passed into an electron pick-up tube into which gas is introduced. Metal foil targets had been tried as electron donor devices but had proved unsuitable. The emergent beam consists of H^-, H^0, H^+ ions and electrons. The electrons are suppressed by a disc maintained at 50 V negative to the pick-up tube and the hydrogen ions, passing through an axial hole in this plate, are accelerated, focused and travel through a magnetic analyser which deflects the negative hydrogen ions through 13° horizontally to strike a Vycor disc inside a Faraday cup. The beam is here measured and analysed and proton formation determined. The resolution is insufficient to distinguish H^- ions from H_2^+ and H_3^+ sources and these, taken together, form the majority of the beam current. An evapor-ion pump is used to maintain a vacuum of below 10^{-4} mm. Hg in the ion source because of its high pumping speed for hydrogen and nitrogen. The pump is similar to that described by Davis and Divatia in 1954, but has been modified to give structural simplicity and long operating life, at the expense of high pumping speed, as hydrogen and nitrogen are pumped by the chemical gettering action of the evaporating titanium. Aluminium gaskets were used on all demountable vacuum joints and the whole of the ion source was made in metal and ceramic to allow the high temperature operation consequent to large power inputs. Hydrogen was the most thoroughly studied target gas. The pick-up tube was made partly of molybdenum and partly of aluminium. The latter softened once, indicating that the temperature rose to about 600°C. This is in agreement with a hydrogen gas temperature of 400°C, required to obtain a gas density consistent with the charge exchange cross-sections quoted by Whittier.

Article by J. A. Weinman & J. R. Cameron *Rev. Sci. Instrum.* **27**, May 1956 288-293

Vacuum Equipment for the 4MeV Linear Electron Accelerator 55/IV

United Kingdom. This report describes the vacuum system of the 4 MeV linear electron accelerator, including the self-contained pumping tables, and the automatic control equipment. An account is given of development work on the diffusion pumps and vacuum gauges and the design of high-vacuum shut-off valves.

(*Authors*)

Report by B. G. Loach *A.E.R.E. Rep.* No. EL/R 299 March 1949 (cleared for sale in 1956)

Compound Ion-Resonance Mass Spectrometer 56/IV

See Abstract No.: 46/II

Gas Counting Techniques in Biochemistry II. 57/IV

See Abstract No.: 7/IV

Improved Methane Proportional Counting Method for Tritium Assay 58/IV

See Abstract No.: 9/IV

Effect of Strain on the Work Function of Polycrystalline Silver 59/IV

United States. The effect of cold work on properties such as conductivity and susceptibility has been investigated, but not the effect on work function. Recent work on vacuum-deposited films of Au and Ag, showing work functions substantially lower than for bulk metal, suggested that there might be some effect. This paper reports the results of measurements on Ag strips before and after stretching beyond the elastic limit. The test strips were 4 × 0.4 × 0.02 cm., mounted between two clamps in a Pyrex tube which could be evacuated. The

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strip could be stretched *in situ* by extending a metal bellows at one end of the tube, to which one clamp was fixed. A tungsten filament was mounted in the tube, close to the strip, so that the latter could be outgassed and annealed by radiation and electron bombardment. The work function was measured by the Kelvin method against a polished Ni reference plate which was mounted on a sliding spindle in a side tube and could be moved up to the Ag strip by a magnet. The electrometer valve and galvanometer forming part of this arrangement had a sensitivity equivalent to 10^{-15} A per mm. Measurements were first made on an electropolished strip in air; after annealing *in vacuo*, the contact potential difference was measured at intervals until the sharp increase observed at first had nearly levelled off. After 73 hr., the strip was stretched in small steps to a total of about 0.25%, which produced a sudden rise in the c.p.d. A further 20 hr. showed only a small change whereas a further stretching gave another discontinuity in the potential/time graph. A total strain of about 1% was associated with an increase in work function of 0.01 eV. A further series of experiments were made with similar strips held in a vacuum of 10^{-6} mm. Hg; after 1 min. at 350°C, the work function rose in about 30 min. to a steady value. Repeated heat treatments showed a small decrease in the steady figure each time, attributed to outgassing. A 2.5% stretching then gave an increase of 0.028 ± 0.002 eV, which was maintained in spite of further heat treatment. In another series, after 7 hr. outgassing at 600°C giving a final vacuum estimated at better than 3×10^{-8} mm. Hg, c.p.d. measurements gave somewhat similar results, a total strain of about 1% giving a change in work function of 0.017 eV. 10 min. at 400°C then gave a reverse change of 0.011 eV—with a further stretching the whole cycle of changes was repeated. A summary of the results is given in a table reproduced below. In the final discussion various structural changes are considered as possible causes of the phenomena observed, but the reversible nature of the changes eliminates many of these. Defects such as vacancies, interstitials and dislocations, which would be reversible, are expected to cause a change in work function of the opposite sign to that observed. It is concluded that the cause of the effect remains uncertain and that precision measurements should be made on well-annealed crystals.

Strip	*Condition of surface*	*Vacuum in mm. Hh*	*Strain in %*	*Change in work function subsequent to stretching in ev.*	*Length treatment in minutes*	*Changes in work function subsequent to heating in ev.*
1	polished	1 atmos	1	0.010	—	—
2	polished	10^{-6}	1.5	0.028	1	—
3	polished	10^{-6}	1	0.027	1	—
4	polished	3×10^{-7}		0.030	10	0.025
5	unpolished	3×10^{-8}	1	0.017	10	0.011
			1	0.016	10	0.010

Article by G. Wallis & H. E. Farnsworth *J. Appl. Phys.* 27, June 1956 594-598

60/IV

Band Spectra Emitted by Strontium and Barium in Arcs and Flames

See Abstract No.: 112/I

61/IV

Spectral Energy Distribution Curves of ZnS: Ag and ZnCdS: Ag after Thermal Vacuum Treatment

See Abstract No.: 70/I

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62/IV

Method of Bonding an Article Thereby Formed

United States. Ultrasonic delay lines used in electronics to delay a signal passed from a driver circuit to a receiver circuit for a short time may consist of a piezo-electric crystal in the driver circuit and a piezo-electric crystal in the receiver circuit both made of quartz, connected by a bar made of glass which is joined and firmly bonded at either end to the respective piezo-electric crystal. Bonding means such as organic cements used in the past have been unstatisfactory for various reasons, for instance incomplete drying out of the interior of the bonding layer and not sufficiently thin bonds. It is proposed to use instead metals which adhere well to the elements being joined as well as to themselves. Indium, gallium, thallium and some of their alloys have adequate adhesion and self-diffusion properties to be suitable for use in the proposed joining technique. The surfaces to be bonded are cleaned and placed in a vacuum chamber. The bonding agent is evaporated from a tungsten filament on to the surfaces and the two coated surfaces are brought together and a pressure of about 1,200 pounds per square inch is applied for between 12 and 24 hours while the components are being kept at a temperature just below the melting point of the deposited material. The bonding layer is preferably very thin, of the order of about 0.001 inch.

D. L. Arenberg *U.S. Pat.* 2,754,238

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A.E.C. Rep.	U.S. Atomic Energy Commission Report, Office of Technical Services, Department of Commerce, Washington 25, D.C., U.S.A.
A.E.R.E. Rep.	U.K. Atomic Energy Research Establishment Report. Harwell, Berks, England. Her Majesty's Stationery Office, P.O. Box No. 569, London, S.E.1., England.
A.I.Ch.E. Journal	American Institute of Chemical Engineers, 25, West 45th Street, New York 36, N.Y., U.S.A.
A.I.M.E.	American Institute of Mining and Metallurgical Engineers Inc., 29, West 39th Street, New York 18, N.Y., U.S.A.
Analyt. Chem.	Analytical Chemistry, American Chemical Society, 20th and Northampton Streets, Easton, Pa., U.S.A.
Ann. Phys.	Annalen der Physik, Johann & Ambrosius Barth, Salomonstrasse 18b, Leipzig C.1, Germany.
Appl. Sci Res.	Applied Science Research, Martinus Nijhoff, The Hague, Holland.
ASEA Journal	Allmanna Svenska Elektriska Aktiebolaget, Vasteras, Sweden.
A.S.T.M.	American Society for Testing Materials 1916, Race Street, Philadelphia 3, Pa., U.S.A.
Atomics	Leonard Hill Ltd., Stratford House, Eden Street, London, N.W.1, England.
Battelle Memorial Inst. Rep.	Battelle Memorial Institute Report, Columbus 1, Ohio, U.S.A.
Battelle Tech. Rev.	Battelle Technical Review, Battelle Memorial Institute, Columbus 1, Ohio, U.S.A.
Bell Tech. J.	Bell System Technical Journal, Bell Telephone Laboratories Inc., 463, West Street, New York 14, N.Y., U.S.A.
B.I.S.R.A.	British Iron and Steel Research Association, 11, Park Lane, London, W.1., England.
Brit. J. Appl. Phys.	British Journal of Applied Physics, Institute of Physics, 47, Belgrave Square, London, S.W.1., England.
Brit. Med. J.	British Medical Journal, British Medical Association, Tavistock Square, London, W.C.1., England.
Bull. Classe. Sci.	Bulletin de la Classe des Sciences, Academie Royale de Belgique, Palais des Academies, 1, Rue Ducale, Brussels, Belgium.
Bull. Inst. Polit.	Bulletin de l'Institut Polytechnique de Jassy, Professor Dr. D. I. Mangeron, Mathematical Institute of the Polytechnical High School of Jassy, Jassy, Roumania.
Bull. School Mines Metall.	Bulletin of School of Mines and Metallurgy, University of Missouri, Rolla, Mo., U.S.A.
Bull. Soc. Chim. France	Bulletin de la Societe Chimique de France, 28, Rue St. Dominique, Paris VII, France.
Canad. J. Phys.	Canadian Journal of Physics, The National Research Council, Ottawa, Canada.
Chem. & Industr.	Chemistry and Industry, Society of Chemical Industry, 56, Victoria Street, London, S.W.1., England.
Chem. Engng.	Chemical Engineering, McGraw-Hill Publishing Co., Inc., 330, West 42nd Street, New York 36, N.Y., U.S.A.
Chem. Engng. Progr.	Chemical Engineering Progress, American Institute of Chemical Engineers, 120, East 41st Street, New York 17, N.Y., U.S.A.
Chem Technik	Chemische Technik, VEB Verlag Technik, Unter Den Linden 12, Berlin, N.W.7., Germany.
Chim. & Industr.	Chimie & Industrie, Edition des Presses Documentaires, 28, Rue Saint-Dominique, Paris VII, France.
Compr. Air Mag.	Compressed Air Magazine, Compressed Air Magazine Co., Phillipsburg, N.Y., U.S.A.
Congres. Intern. Verre	Congres International du Verre, Institut National du Verre, 24, Rue Dourlet, Charleroi, Belgium.
C.R. Acad. Sci. Paris	Comptes Rendus des Séances de l'Academie des Sciences, Messrs. Gauthier-Villar, 55, Quai des Grands-Augustine, Paris, France.
Czechosl. J. Phys.	Czechoslovak Journal of Physics, Ustav technicke fysiky CSAV, Cukrovarnicka 10, Praha 5, Czechoslovakia.
Discovery	Jarrold & Sons, Ltd., London Street, Norwich, England.
Elect. J.	The Electrical Journal, Bouverie House, 154, Fleet Street, London, E.C.4., England.
Elect. Rev.	Electrical Review, Electrical Review Publications, Ltd., Dorset House, Stamford Street, London, S.E.1., England.

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Electro. Metal Finish.	Electroplating and Metal Finishing, 85, Udney Park Road, Teddington, Middlesex, England.
Elect. World	Electrical World, McGraw Hill Publishing Co., Inc., 330, West 42nd Street, New York, 36, N.Y., U.S.A.
Elektrotech Z.	Electrotechnische Zeitschrift, Verband Deutscher Elektrotechniker (VDE) Verlag, Wuppertal, Germany.
Endeavour	Imperial Chemical Industries Ltd., 26, Dover Street, London, W.1., England.
Engineer	The Engineer, Morgan Brothers (Publishers), Ltd., 28, Essex Street, Strand, London, W.C.2., England.
Engineering	Engineering Ltd., 35-36, Bedford Street, London, W.C.2., England.
Food	Tothill Press Ltd., 33, Tothill Street, London, S.W.1., England.
Food Engng.	Food Engineering, McGraw-Hill Publishing Co., Inc., 330, West 42nd Street, New York 36, N.Y., U.S.A.
Food Manuf.	Food Manufacture, Leonard Hill Ltd., 17, Stratford Place, London, W.1., England.
Foundry	Penton Publishing Co., Penton Building, Cleveland 13, Ohio, U.S.A.
Foundry Trade J.	Foundry Trade Journal, John Adams House, 17-19, John Adams Street, Adelphi, London, W.C.2., England.
Fruits	Fruits D'Outre Mer, Institut Français de Recherches Fruitieres Outre-Mer (I.F.A.C.), 6, Rue de General-Clergiere, Paris XVI, France.
Galvano	79, Avenue des Champs-Elysées, Paris VIII, France.
Gen. Chim.	Genie Chimique, Edition des Presses Documentaires, 28, Rue Saint-Dominique, Paris VII, France.
Giesserei	Giesserei Verlag G.m.b.H., Düsseldorf, Germany.
Helv. Phys. Acta.	Helvetica Physica Acta, Physikalische Anstalt, Universität, Klinverbergstrasse 82, Basle, Switzerland.
Hüttenzeit.	Hüttenzeitung, Bochumer Verein für Gusstahlfabrikation A.G. Kohlenstrasse 70, Bochum, Germany.
Industr. Engng. Chem.	Industrial Engineering Chemistry, American Chemical Society, 20th and Northampton Streets, Easton, Pa., U.S.A.
Industr. Finish.	Industrial Finishing, Arrow Press Ltd., 157, Hagden Lane, Watford, Herts, England.
Ingen. Tech.	Ingénieurs et Techniciens, 30, Rue Tronchet, Paris IX, France.
Inst. Min. Metall.	Institute of Mining and Metallurgy, 44, Portland Place, London, W.1., England.
Ion	18-20, Paseo del Prada, Madrid, Spain.
Iron Age	Chilton Co., Inc., Chestnut and 56th Street, Philadelphia 39, Pa., U.S.A.
Iron & Steel	The Louis Cassier Co., Ltd., Dorset House, Stamford Street, London, S.E.1., England.
J. Appl Phys.	Journal of Applied Physics, American Institute of Physics, 57, East 55th Street, New York 22, N.Y., U.S.A.
J. Bone & Joint Surgery	Journal of Bone and Joint Surgery, 8, The Fenway, Boston 15, Massachusetts, U.S.A.
J. Chem Educ.	Journal of Chemical Education, Div. of Chemical Education of the American Chemical Society, Scripps Institution, La Jolla, California, U.S.A.
J. Electrochem. Soc.	Journal of the Electrochemical Society. The Electrochemical Society, 235, West 102nd Street, New York 25, N.Y., U.S.A.
J. Electronics	Journal of Electronics, Taylor & Francis Ltd., 18, Red Lion Court, Fleet Street, London, E.C.4., England.
J. Hygiene	Journal of Hygiene, 200, Euston Road, London, N.W.1., England.
J. Inst. Brewing	Journal of the Institute of Brewing, Institute of Brewing, 33, Clarges Street, London, W.1., England.
J. Inst. Metals	Journal of the Institute of Metals, The Institute of Metals (Inc)., 17, Belgrave Square, London, S.W.1., England.
J. Iron Steel Inst.	Journal of the Iron and Steel Institute, Iron and Steel Institute, 4, Grosvenor Gardens, London, S.W.1., England.
J. Japanese Vac. Soc.	Mr. S. Asao, Matsuda Research Laboratory, Tokyo Shibaura Electric Co., 72, Horikawa-Cho, Kawasaki-Shi, Kanagawa-Ken, Japan.
J. Metals	Journal of Metals, American Institute of Mining and Metallurgical Engineers Inc., 29, West 39th Street, New York 18, N.Y., U.S.A.

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J. Nuclear Energy	Journal of Nuclear Energy, Pergamon Press Ltd., 4-5, Fitzroy Square, London, W.1., England.
J. Opt. Soc. Amer.	Journal of the Optical Society of America, American Institute of Physics, 57, East 55th Street, New York 22, N.Y., U.S.A.
J. Photo. Sci.	The Journal of Photographic Science, Royal Photographic Society, 16, Princess Gate, London, S.W.7., England.
J. Phys. Chem.	Journal of Physical Chemistry, American Chemical Society, 1155, Sixteenth Street, N.W., Washington 6, D.C., U.S.A.
J. Phys. Radium	Le Journal de Physique et le Radium, La Societé Française de Physique, 10, Rue Vauquelin, Paris V, France.
J. Sci. Instrum.	Journal of Scientific Instruments, Institute of Physics, 47, Belgrave Square, London, S.W.1., England.
J. Soc. Dyers & Colourists	Journal of Society of Dyers and Colourists, 19, Piccadilly, Bradford, England.
J.S.M.P.T.E.	Journal of the Society of Motion Picture and Television Engineers, Society of Motion Picture and Television Engineers, 40, West 40th Street, New York 18, N.Y., U.S.A.
J. Soc. Glass Technol.	Journal of the Society of Glass Technology, 'Elmfield', Northumberland Road, Sheffield, England.
Lab. Practice	Laboratory Practice, United Trade Press Ltd., 9, Gough Square, Fleet Street, London, E.C.4., England.
Light Metals	Temple Press Ltd., Bowling Green Lane, London, E.C.1., England.
Mater. & Meth.	Materials and Methods, 330, West 42nd Street, New York 36, N.Y., U.S.A.
Mech. World	Mechanical World, Kennedy Press Ltd., 31, King Street West, Manchester 3, England.
Metal Finish.	Metal Finishing, Finishing Publications Inc., 11, West 42nd Street, New York 19, N.Y., U.S.A.
Metall. Rev.	Metallurgical Review, Institute of Metals, 17, Belgrave Square, London, S.W.1., England.
Metal Progr.	Metal Progress, American Society of Metals, 7301, Euclid Avenue, Cleveland 3, Ohio, U.S.A.
Met. Corr. Industr.	Metaux Corrosion Industries, Editions Metaux, 32, Rue du Maréchal-Joffre, Saint-Germain-en-Laye,
Mfg. Chem.	Manufacturing Chemist, Leonard Hill Ltd., Stratford House, 9, Eden Street, London, N.W.1., England.
Modern Metals	Modern Metals Publishing Co., 206, South Michigan Ave., Chicago 4, Ill., U.S.A.
Mod. Refrig.	Modern Refrigeration, Refrigeration House, Victoria Road, Woking, Surrey, England.
Municipal J.	The Municipal Journal, Municipal Journal Limited., 3, Clements Inn, London, W.C.2., England.
Metal Industr.	Metal Industry, Iliffe & Sons, Ltd., Dorset House, Stamford Street, London, S.E.1., England.
N.A.C.A. Rep.	National Advisory Committee for Aeronautics Report, Washington D.C., U.S.A.
Nachrichtentech.	Nachrichtentechnik, Verlag Technik, Unter den Linden, 12, Berlin N.W.7., Germany.
Nature	Macmillan & Co., St. Martin's Street, London, W.C.2., England.
Nucleonics	McGraw-Hill Publishing Co., Inc., 330, West 42nd Street, New York 36, N.Y., U.S.A.
Onderstepoort J. Vet. Res.	Onderstepoort Journal of Veterinary Research, Government Printer, Pretoria, S. Africa.
Optica Acta	International Commission of Optics, 3, Boulevard Pasteur, Paris XV, France.
Petrol. Ref.	Petroleum Refiner, The Gulf Publishing Co., Box 2608, Houston 1, Texas, U.S.A.
Philips Res. Rep.	Philips Research Report, Philips Electrical Ltd., Century House, Shaftesbury Avenue, London, W.C.2., England.
Philips Tech. Rev.	Philips Technical Review, Philips Electrical Ltd., Century House, Shaftesbury Avenue, London, W.C.2., England.
Philos. Mag.	Philosophical Magazine, Taylor & Francis Ltd., 18, Red Lion Court, Fleet Street, London, E.C.4., England.
Phys. Rev.	Physical Review, American Institute of Physics, Brookhaven National Laboratory, Upton, Long Island, N.Y., U.S.A.

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P.M.M.	Precision Metal Molding, Industrial Publishing Corp., 812, Huron Road, Cleveland, Ohio, U.S.A.
Powder Metall. Bull.	Powder Metallurgy Bulletin, Metallwerk Plansee G.m.b.H., Reutte/Tyrol, Austria.
Pre Pack Age	Cooper Publishing Co., Inc., 500, Fifth Avenue, New York 36., U.S.A.
Proc. Control Autom.	Process Control and Automation, 30 & 31, Furnival Street, London, E.C.4., England.
Proc. Phys. Soc.	Proceedings of the Physical Society, The Physical Society, 1, Lowther Gardens, Prince Consort Road, London, S.W.7., England.
Prod. Engng.	Product Engineering, McGraw-Hill Publishing Co., Inc., 330, West 42nd Street, New York 36 N.Y., U.S.A.
Quart. J. Micros. Sci.	Quarterly Journal of Microscopical Science, Clarendon Press, Oxford, England.
Research	Butterworths Scientific Publications, 4-6, Bell Yard, Temple Bar, London, W.C.2., England.
Rev. Metall.	Revue de Metallurgie 5, Cité Pigalle, Paris V, France.
Rev. Opt.	Revue d'Optique, 3-5, Boulevard Pasteur, Paris XV, France.
Rev. Sci. Instrum.	Review of Scientific Instruments, American Institute of Physics, 57, East 55th Street, New York 22, N.Y., U.S.A.
Science	American Association for the Advancement of Science, 1515, Massachusetts Avenue, N.W., Washington 5, D.C., U.S.A.
Sci. Progr.	Science Progress, Edward Arnold (Publishers), Ltd., 41, Maddox Street, London, W.1., England.
Stahl u.Eisen	Stahl und Eisen, Düsseldorf, Germany.
Steam Engr.	The Steam Engineer, John D. Troup Limited, 90, High Holborn, London, W.C.1., England.
Steel	Penton Publishing Co., Penton Building, Cleveland 13, Ohio, U.S.A.
Times Rev. Industr.	The Times Review of Industry, The Times Publishing Co., Ltd., Printing House Square, London, E.C.4., England.
Times Sci. Rev.	Times Science Review, The Times Publishing Co., Ltd., Printing House Square, London, E.C.4., England.
Trans. Faraday Soc.	Transactions of the Faraday Society, Aberdeen University Press Ltd., 6, Upper Kirkgate, Aberdeen, Scotland.
Upsekhi Fizicheskikh Nauk	Gosudarstvennoe Izadtel'stvo Tekniko-Teoreticheskoi Literatury, Moscow, Russia.
U.S. Dept. Air Force Rep.	U.S. Department of the Air Force Report, Superintendent of Documents, U.S. Government Printing Office, Washington, 25, D.C., U.S.A.
U.S. Naval Ordnance Lab. Rep.	U.S. Naval Ordnance Laboratory Report, U.S. Department of Commerce, Office of Technical Services, Washington 25, D.C., U.S.A.
U.S. Naval Research Lab. Rep.	U.S. Naval Research Laboratory Report, U.S. Department of Commerce, Office of Technical Services, Washington 25, D.C., U.S.A.
Vakuum-Tech.	Vakuum-Technik, Rudolf A. Lang Verlag, Leibnizstrasse 64, Berlin-Charlottenburg 4, Germany.
Le Vide	Societé Française des Ingénieurs des Techniciens du Vide, 44, Rue de Rennes, Paris VI, France.
Westinghouse Engr.	Westinghouse Engineer, Westinghouse Electric Corp., 306, Fourth Avenue, P.O. Box 1017, Pittsburgh 30, Pa., U.S.A.
World's Paper Trade Rev.	World's Paper Trade Review, Stonehill and Gillis Ltd., 329, High Holborn, London, W.C.1., England.
Z. Angew. Phys.	Zeitschriften für Angewandte Physik, Springer Verlag, Jebenstrasse 1, Berlin-Charlottenburg, Germany.
Z. Metallkde.	Zeitschrift für Metallkunde, Dr. Riederer-Verlag G.m.b.H., Marienstrasse 50, Stuttgart W., Germany.
Z. Naturforsch.	Zeitschrift für Naturforschung, Verlag der Z. für Naturforschung, Mathildenstrasse 29, Tübingen, Germany.

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